Volume 19 . No. 11

Nov. 1949

JOURNAL OF GENERAL CHEMISTRY of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN

c/b CONSULTANTS BUREAU, NEW YORK

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THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Vol. 19, 1949

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THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Vol. 19 (1949)

No. 11, November

Technical Editor: A.B. Smyrnova

Publication of the Academy of Sciences of the U. S. S. R.

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU
153 West 33 Street
New York 1, N.Y.

Printed in the United States of America.

Annual subscription $95.00. Single copy $12.00.

ALEXANDER NIKOLAYEVICH NESMEYANOV

(On his 50th Birthday)

L. G. Makarova and A. E. Borisov

September 9, 1949 marks the 50th birthday of the eminent Soviet chemist, Academician Alexander Nikolayevich Nesmayanov, the author of classical works in the field of element-organic compounds and the founder of an extensive chemical school. A great scientist, paving new roads in science, a remarkable educator and trainer of the new generation, A.N.Nesmeyanov is also an outstanding organizer and a civic leader.

A.N.Nesmeyanov was born on September 9 (August 28), 1899 in Moscow, the son of N.V.Nesmeyanov, a school teacher. After completing the Strakhov gymnasium in Moscow in 1917, he matriculated in the physical-mathematical faculty of the first Moscow State University, graduating in 1932. While still a student, Alexander Nikolayevich attracted the attention of N.D.Zelinsky by his profound erudition and independent thinking, and at the latter's suggestion he was appointed to a fellowship by the university and engaged as research worker in the laboratory of organic and analytical chemistry, directed at that time by Zelinsky. In Zelinsky's laboratory Alexander Nikolayevich commenced his research on the esters of complex acids, which subsequently resulted in his discovery of the diazo method of synthesizing metallo-organic compounds. In 1924, Alexander Nikolayevich began his pedagogical career as an assistant to N.D.Zelinsky's chair, directing the students' laboratory training in qualitative analysis; later, he was in charge of their laboratory work in organic chemistry. From the very start of his teaching career, A.N.Nesmeyanov displayed his superior pedagogical talents.

Alexander Nikolayevich was soon appointed an instructor, and in 1935 he won his doctorate in chemical sciences and was named a professor. He was appointed a professor of the faculty of chemistry of Moscow State University that same year.

Parallel with his work at the university, Alexander Nikolayevich organized a laboratory of organic chemistry in the Institute of Insectofungicides, where he and his associates carried out much research on the diazo synthesis of metallo-organic compounds and on organofluoric compounds, and proposed a number of valuable practical agents to combat plant pests. Alexander Nikolayevich directed this laboratory until 1935, when he was asked to organize a laboratory of metallo-organic compounds in the newly established Institute of Organic Chemistry of the USSR Academy of Sciences in Moscow; he has been the director of this laboratory down to the present time. In this laboratory the chemistry of quasicoordination compounds has been elaborated, and research has been done on the synthesis of metallo-organic compounds, the decomposition of such compounds, and a whole series of extremely valuable other research projects.

In 1938 Alexander Nikolayevich was appointed to the chair of organic chemistry of the Institute of Precise Chemical Technology, where he also carried on considerable research work. He occupied this chair until his evacuation to Kazan with the Institute of Organic Chemistry of the Academy of Sciences during the war,

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in July, 1941.

In 1939 Alexander Nikolayevich was elected a corresponding member of the USSR Academy of Sciences as well as Director of the Institute of Organic Chemistry. He still is the director of this institute.

During the war the Institute of Organic Chemistry of the Academy of Sciences and the laboratories supervised by Alexander Nikolayevich did work of especial practical importance. Recognition of Alexander Nikolayevich's scientific services resulted in his election to full membership in the USSR Academy of Sciences in 1943. In 1944 Alexander Nikolayevich occupied the chair of organic chemistry in the faculty of chemistry of Moscow State University, where he now lectures in the basic course on organic chemistry and supervises the work done for their theses by students and the research work of the fellows, assistants, and instructors attached to the chair. A brilliant lecturer, Alexander Nikolayevich has the knack of combining scientific rigor with simplicity and charm. His lectures always attract a large audience, not only of second- and third-year students, for whom they are planned, but of fellows, instructors, and research workers as well.

In 1945 Alexander Nikolayevich was named dean of the chemistry faculty of Moscow State University and immediately went to work on the re-establishment of scientific research in the faculty. In Autumn 1945, Alexander Nikolayevich was sent to Paris as a delegate to the congress of the French Association for the Advancement of Science. During his stay of a month, he took the opportunity of acquainting himself with the educational setup and the organization of scientific research in the Paris institutions of higher learning and research institutes.

In 1946 Alexander Nikolayevich was elected Academician-Secretary of the Division of Chemical Sciences and a member of the Presidium of the Academy of Sciences. In 1944 he had been named a member of the Stalin Prize Committee for Science and Inventions attached to the Council of Ministers of the USSR and vice-chairman of its chemistry section, and in 1946 he was appointed chairman of the Stalin Prize Committee. In the summer of 1947, Alexander Nikolayevich took part in the International Chemistry Congress in London.

His outstanding talents as an organizer advanced A.N.Nesmeyanov in 1947 to the post of rector of the oldest university in Russia, the M.V.Lomonosov Moscow State University. In the spring of 1948 Alexander Nikolayevich headed the Soviet delegation at the celebration of the 600th anniversary of the Charles University in Prague, and in the autumn of the same year he was commissioned to go to Krakow to attend the jubilee of the Polish Academy of Sciences. In 1949 he was elected an honorary member of the Polish Chemical Society.

Alexander Nikolayevich is a member of the editorial boards of a number of periodicals: The Journal of General Chemistry, Izvestia of the Academy of Sciences, and the Moscow University Herald. During the war, the publishing house of the USSR Academy of Sciences began publication, under the joint editorship of A.N. Nesmeyanov and K.A.Kocheshkov, of a series of monographs: Synthetic Methods in the Field of Metallo-Organic Compounds, in which world research and experiment in this field and the research work of the laboratories headed by Nesmeyanov and Kocheshkov were brought together.

In addition to the tremendous load he carries in Moscow State University and the USSR Academy of Sciences, Alexander Nikolayevich is engaged in much governmental work: he is a vice-chairman of the Supreme Soviet of the RSFSR and a deputy to the Supreme Soviet of the RSFSR representing the Kemerovo Region.

A.N.Nesmeyanov's outstanding achievements have received high recognition from

the government; he has been awarded the Order of Lenin twice: in 1944 for his success in training personnel, and in 1945 on the occasion of the 220th Anniversary of the Academy of Sciences. He has also been decorated with the Medal "For Valiant Work During the Great Patriotic War" and the Medal "In Commemoration of Moscow's 800th Anniversary." Alexander Nikolayevich is a winner of the Stalin Prize, First Class.

In view of the impossibility of describing the scientific activity of A.N. Nesmeyanov in any detail in so short a review, we shall confine ourselves to a brief summary of his most important fields of research.

Alexander Nikolayevich's scientific work has been done on the chemistry of metallo-organic compounds. Notwithstanding the fact that the chemistry of metallo-organic compounds has a glorious history of one hundred years, and that so many fruitful syntheses of metallo-organic compounds were introduced into organic chemistry 50 to 70 years ago, it was only at the time of World War I that individual representatives of the metallo-organic compounds found practical application, though only of accidental nature. Systematic, extensive application and study of the metallo-organic compounds had been retarded by the absence of convenient and universal methods of synthesizing them. Often the simplest reactions were unstudied, the simplest types of substances were inaccessible owing to the impossibility of their synthesis.

Elaborating methods of synthesis was the most urgent problem of the chemistry of metallo-organic compounds. That is why Alexander Nikolayevich's creation in 1929 of the diazo method of synthesizing these compounds, first developed by him for the organo-mercuric compounds, which are the keys to the metallo-organic compounds, was an important contribution to science. The organic compounds of many elements in the Periodic Table were first prepared via the organomercuric compounds, and many of them are still so synthesized. In 1928 Alexander Nikolayevich investigated the mechanism of the decomposition of double salts of phenyldiazonium iodide and mercuric iodide [1]. Turning to a study of the decomposition of double salts of an aryldiazonium chloride and corrosive sublimate, Alexander Nikolayevich discovered a new, convenient, and universal method for the synthesis of aromatic organomercuric compounds, which by now has become a classic -- the diazo method of synthesizing organomercuric compounds. This method involves the following: the decomposition of a double salt of an aryldiazonium chloride and mercuric chloride by copper powder in acetone, ethyl acetate, or alcohol yields an organo-mercuric salt: $ArN_2Cl \cdot HgCl_2 + 2Cu \longrightarrow ArHgCl + 2CuCl + N_2$. Changing the conditions slightly, namely, performing the reaction with an excess of copper and adding aqueous ammonia, leads directly to the synthesis of fully substituted organomercuric compounds:

$$2ArN_2Cl \cdot HgCl_2 + 6Cu + 6\underline{n}NH_3 \rightarrow Ar_2Hg + 6CuCl + \underline{n}NH_3 + 2N_2 \text{ [3]}.$$

The diazo method makes it possible to combine examples of the most varied classes of aromatic organic compounds with mercury [4], including those with negative substituents in the ring [5]. The method was also applied to heterocyclic compounds [6]. A variant of the diazo method of synthesizing organomercuric compounds was developed, consisting of the decomposition of mercury arylazocarboxylates, [7]. At the present time the method of double diazonium salts is the best method for synthesizing individual aromatic compounds of mercury, since, starting with easily available substances (amines), it gives a high yield, is extraordinarily simple in operation, enables the synthesis of compounds with various substituents, and produces a pure compound, free from isomers. At the present time this method has won wide acceptance, being preferred to other methods of synthesizing aromatic organomercuric compounds.

The feasibility of synthesizing various groups of organo-mercuric compounds, opened up by the diazo method, made it possible to employ these compounds to synthesize and study previously unknown types of aromatic compounds of zinc [8], tin [9], and aluminum [10] with ring substituents. The diazo method was soon extended by A.N.Nesmeyanov, at times in collaboration with K.A.Kocheshkov, to the synthesis of organic compounds of other metals as well: tin [11], antimony [12], and lead [13]. The diazo method of synthesis developed by Alexander Nikolayevich was employed by Soviet and foreign authors to synthesize organic compounds of bismuth [14] and copper [15]. And it is beyond doubt that the possible applications of the method of double diazonium salts are far from exhausted. Research on the diazo method stimulated research by other authors, alongside the research work of Alexander Nikolayevich [16], devoted to ascertaining the mechanism of this reaction.

Developing his research on the diazo method and with a view to clearing up its mechanism, Alexander Nikolayevich has recently engaged in a study of the decomposition of the onium salts in general. It was shown that the homolytic decomposition of diazonium and iodonium salts known in the literature was not the only possible kind, but that, by selecting the proper anion of the salts of onium bases, it was possible to effect the heterolytic decomposition of these salts, forming a positively charged aryl radical. The decomposition of a hydrofluoboric onium salt is of this latter type [17]. The orientation of the aryl group that enters the benzene ring, containing Class I or II orienting groups (or that enters the pyridine ring) is an indication of one type of decomposition or the other and of the shift of the aryl group. Whereas a neutral aryl group enters at the ortho or para position with any orienting group (Class I or II) (or at the α,β-position in pyridine), a positively charged aryl group enters at the meta position in the benzene ring that contains a meta orienting group (nitrobenzene, ethyl benzoate, phenyltrimethylammonium borofluoride, and benzotrifluoride), is subject to the usual orientation in the benzene ring produced by a Class II orienting group, and is attached at the free pair of electrons to pyridine's nitrogen (as well as to the nitrogen of trimethylamine, the phosphorous of triphenylphosphine, the arsenic in triphenylarsine, etc.).

Elucidation of the mechanism of the decomposition of onium compounds makes it possible to control syntheses (especially of metallo-organic compounds) by means of these compounds and explains the tautomeric shift of the diazonium form to the diazo form under the influence of carriers of free electron pairs: the hydroxyl ion, amines and the cyanogen ion. The decomposition of diphenyliodonium borofluoride may be employed as a method of arylation.

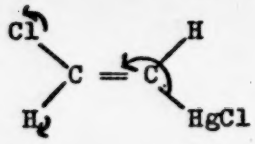
Thus, the significance of the diazo method of synthesizing metallo-organic compounds discovered by A.N.Nesmeyanov is not confined to an excellent method of synthesizing the organic compounds of mercury, tin, antimony, lead, bismuth and copper (as well as of various organic compounds of other metals, using these metallo-organic compounds as intermediates); this discovery gave rise to a large number of research projects, which in turn provided chemistry with new methods of synthesis and enriched the science with new concepts.

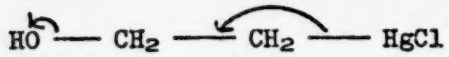
Paralled to his work on the diazo method, Alexander Nikolayevich elaborated a number of other synthesis methods in the field of element-organic compounds: he set forth a new and original method for synthesizing organomercuric compounds by the arylation of mercuric oxide by iodine compounds [18]. A new method of synthesizing organostannic compounds by reducing organomercuric compounds with salts of bivalent tin was developed by A.N.Nesemyanov in collaboration with K.A. Kocheshkov [19]. Research was done on the arylation of corrosive sublimate and mercuric oxide by aromatic compounds of tin, lead, arsenic, and antimony [20];

resulting in the discovery of a new method of synthesizing asymmetrical organomercuric compounds [21].

Long before the broad development of the chemistry of organofluoric compounds, Alexander Nikolayevich developed a new and highly valuable method for synthesizing the acid fluorides of carboxylic acids, involving the reaction of a carboxylic acid with potassium fluoride in the presence of the acid chloride [22]; this yielded formyl fluoride - the only acid halide of formic acid synthesized up to the present time. A.N.Nesmeyanov and K.A.Kocheshkov evolved an original method for the synthesis of tungsten and molybdenum carbonyls by the action of carbon monoxide in the presence of zinc dust [23]. They did research on the reaction of nitrogen oxide and trioxide with metallo-organic compounds, a reaction that is the inverse of the diazo method of synthesizing metallo-organic compounds [24].

A broad field in which detailed research has been done by A.N.Nesmeyanov and his pupils is the quite singular chemistry of the addition products of metallic salts and unsaturated compounds, such as acetylene and ethylene and their derivatives and carbon monoxide. What is remarkable about these substances is the fact that in their chemical reactions they exhibit a striking dual behavior, resembling the dual reactions of tautomeric compounds. At times they react as true metallo-organic compounds, formed by the addition of a metallic salt to the multiple bond of an unsaturated molecule, but at other times they enter into reaction as complex addition compounds of metallic salts and the unsaturated compound. Such compounds were accordingly called quasicomplex compounds by Alexander Nikolayevich. For a long time the question of the structure of addition products of mercury and the olefins remained unsettled and was the subject of prolonged discussion between the adherents of their truly metallo-organic nature and the champions of their coordination structure. In his fundamental research Nesmeyanov demonstrated the structure of these compounds and of addition products of metallic salts with triple bonds, providing a unified explanation of the reasons for their quasicomplex properties. Both the literature data and Alexander Nikolayevich's own research [25] on the synthesis and the study of the reactivity of the addition products of mercury salts and various derivatives of ethylene served as experimental bases for the proof of the structure of addition products of metallic salts and the olefins. Alexander Nikolayevich devoted an entire research cycle to a study of the addition products of metallic salts and acetylene. Detailed investigations demonstrated that the addition products of mercury salts [26], and of the salts of tin [27], antimony [28], thallium [29], lead [30], and iodine [31] with acetylene, which Alexander Nikolayevich and his associates were the first to synthesize, clearly exhibit the dual behavior that is characteristic of quasicomplex compounds. Alexander Nikolayevich was the first to succeed in isolating stable trans and cis isomers of all these compounds. In a series of exquisite investigations he effected the transfer of the vinyl chloride group from one metal atom to another and faultlessly proved that this transfer takes place without changing the geometrical configuration of the radical [32]. This conversion of the trans isomer into the cis isomer, accomplished for vinyl chloride derivatives of mercury and tin takes place only under ultraviolet irradiation [33] and under the action of peroxides [34]. The existence of stable trans and cis isomers does not permit us to ascribe the duality of reaction of these compounds to tautomerism or to the existence of a labile equilibrium of the addition compound with its dissociation products, but compels us to assign a single structure formula to each of these substances. His profound knowledge of the properties of quasicomplex compounds led Alexander Nikolayevich to the conclusion that the singular properties of these compounds – the ease with which acetylene and the olefin are eliminated, resembling the ionic state of a metal and the anion portion of an addition compound – are due to conjugated single bonds, as expressed by formulas of this type:





He explained the properties of the recently synthesized acetaldehydemercury chloride as also due to conjugation of both single and double bonds [36]. Alexander Nikolayevich cited arguments to show that the conjugation of single bonds and of single and double bonds is the result of polarizability [37]. He extended the concept of the transfer of the reactive center of the molecule as the result of conjugation, which was based upon study of the properties of quasicomplex compounds, to elucidating the dual nature of the reactions of metallic derivatives of keto-enols, lactim-lactams, and similar compounds, and – more broadly – to the general case of transferring the reactivity of the key atoms from one molecule to another. The explanation of the dual reactivity of metallic derivatives of tautomeric prototropic systems, which is based upon investigation of the reactions of C-metallic derivatives of oxo compounds, has now been founded by Alexander Nikolayevich upon the example of their O-metallic derivatives [38].

Endeavoring, like the classics of the chemistry of metallo-organic compounds, to extend the laws discovered in studying these compounds to organic chemistry as a whole, A.N.Nesmeyanov expressed the opinion (which has been successfully corroborated by a wide research program that has now been set up) that conjugated single bonds exist throughout organic chemistry.

LITERATURE CITED *

[1] A.N.Nesmeyanov, Z. anorg. allg. Chem., 178, 300 (1929).

[2] A.N.Nesmeyanov, Jour. Russ. Phys. Chem. Soc., 61, 1393 (1929); Ber., 62, 1010 (1929).

[3] A.N.Nesmeyanov and E.I.Kan, J. Russ. Phys. Chem. Soc., 61, 1407 (1929); Ber., 62, 1018 (1929).

[4] Cf.e.g.: A.N.Nesmeyanov and L.G.Makarova, J. Gen. Chem., 1, 598 (1931); A.N.Nesmeyanov and E.M.Torppova, J. Gen. Chem., 4, 664 (1934); I.T.Eskin and A.N.Nesmeyanov, Izvest. Akad. Nauk, USSR., 1942, 116.

[5] A.N.Nesmeyanov, N.F.Glushnev, N.F. Epifansky, and A.I.Flegontov, J. Gen. Chem., 4, 713 (1934).

[6] A.N.Nesmeyanov and I.F.Lutsenko, J. Gen. Chem., 11, 382 (1941).

[7] A.N.Nesmeyanov and O.A. Reutov, Izvest. Akad. Nauk USSR, 1948, 316.

[8] A.N.Nesmeyanov, K.A. Kocheshkov, and V.I.Potrosov, Sci. Papers of Moscow State Univ., 305 (1934); Ber, 67, 1138 (1934);

[9] A.N.Nesmeyanov and K.A.Kocheshkov, J. Gen. Chem., 1, 19 (1931); Ber., 64, 628 (1931). A.N.Nesmeyanov, K.A.Kocheshkov, and V.P. Puzyreva, J. Gen. Chem., 7, 118 (1937); Ber., 69, 1639 (1938).

[10] A.N.Nesmeyanov and N.N.Novikova, Izvest. Akad. Nauk USSR, Classe Chem. Sci., 1942, 372.

[11] A.N.Nesmeyanov, K.A.Kocheshkov, and V.A.Klimova, J. Gen. Chem., 6, 167 (1936); Ber., 68, 1877 (1935).

[12] A.N.Nesmeyanov and K.A.Kocheshkov, Izvest. Akad Nauk, USSR, Div. Chem. Sci., 1944, 416; Gilman, Svigoon, J. Am. Chem. Soc., 61, 3586 (1939).

* This list does not include all of the published papers of A.N. Nesmeyanov, which comprises some 150 titles.

[13] A.N.Nesmeyanov, K.A.Kocheshkov, and N.K.Gipp, J. Gen. Chem., 6, 167 (1936); A.N.Nesmeyanov, K.A.Kocheshkov, and M.M.Nad, Izvest. Akad. Nauk, Div. Chem. Sci., 1945, 522.

[14] T.K.Kozminskaya, M.M.Nad, and K.A.Kocheshkov, J. Gen. Chem., 16, 1897 (1946).

[15] Bolth, Whalcy, Starkey, J. Am. Chem. Soc., 53, 319 (1931).

[16] A.N.Nesmeyanov, Sci. Papers of Moscow State Univ., 291 (1934).

[17] L.G.Makarova and A.N.Nesmeyanov, Izvest. Akad. Nauk, Div. Chem. Sci. 1945, 617; A.N.Nesmeyanov and L.G.Makarova, Izvest. Akad. Nauk, Div. Chem. Sci., 1947, 213.

[18] A.N.Nesmeyanov and L.G.Makarova, J. Gen. Chem., 3, 257 (1933); Ber., 66, 199 (1933).

[19] A.N.Nesmeyanov and K.A.Kocheshkov, J. Russ. Phys. Chem. Soc., 62, 1795 (1930); Ber., 63, 2396 (1930).

[20] K.A.Kocheshkov and A.N.Nesmeyanov, J. Gen. Chem., 4, 1102 (1934); Ber., 67, 317 (1934).

[21] R.K.Freidlina, K.A.Kocheshkov, and A.N.Nesmeyanov, J. Gen. Chem., 5, 117 (1935); Ber., 68, 565 (1935).

[22] A.N.Nesmeyanov and E.I.Kan, J. Gen. Chem., 4, 1243, 1247 (1934).

[23] K.A.Kocheshkov, A.N.Nesmeyanov, M.M.Nad, I.M.Rossinskaya, and L.M. Borisova, Doklady Akad. Nauk, 1940, 53; K.N.Anisimov and A.N.Nesmeyanov, Doklady Akad. Nauk, 1940, 57.

[24] L.G.Makarova and A.N.Nesmeyanov, J. Gen. Chem., 9, 771 (1939).

[25] A.N.Nesmeyanov and R.K.Friedlina, J. Gen. Chem., 7, 43 (1937); Ber., 69, 1631 (1936); R.K.Freidlina, A.N.Nesmeyanov, and F.A.Tokareva, J. Gen. Chem., 7, 262 (1937); Ber., 69, 2019 (1936); A.N.Nesmeyanov and R.K.Freidlina, J. Gen. Chem., 7, 2748 (1937); A.N.Nesmeyanov and I.F.Lutsenko, Izvest. Akad. Nauk, Div. Chem. Sci., 1942, 366; A.N.Nesmeyanov and I.F.Lutsenko, Izvest. Akad. Nauk, Div. Chem. Sci., 1943, 296.

[26] A.N.Nesmeyanov and R.K. Freidlina, Doklady Akad. Nauk., 26, 59 (1940); Izvest. Akad. Nauk. Div. Chem. Sci., 1945, 151; A.N.Nesmeyanov, A.E.Borisov, and A.N.Guskova, Ibid., 1945, 639.

[27] A.N.Nesmeyanov, A.E.Borisov, and A.N.Abramova, Ibid., 1946, 547.

[28] A.N.Nesmeyanov and A.E.Borisov, Izvest. Akad. Nauk, Div. Chem. Sci., 1945, 251.

[29] R.K.Freidlina, A.K.Kochetkov, and A.N.Nesmeyanov, Izvest. Akad. Nauk., Div. Chem. Sci., 1948.

[30] A.N.Nesmeyanov, R.K.Freidlina, and A.K.Kochetkov, Izvest. Akad. Nauk, 1948.

[31] A.N.Nesmeyanov and R.K.Freidlina, Izvestia Akad. Nauk., Div. Chem. Sci. 1943, 152; R.K.Freidlina, E.M.Brainina, and A.N.Nesmeyanov, Ibid., 1945, 647.

[32] A.N.Nesmeyanov and A.E. Borisov, Doklady Akad. Nauk, 1948, 67.

[33] A.N.Nesmeyanov and A.E.Borisov, Izvest. Akad Nauk, Div. Chem. Sci., 1947, 289; A.N.Nesmeyanov, A. E. Borisov, and A.N.Abramova, Ibid, 1949.

[34] A.N. Nesmeyanov, A.E.Borisov, and V.D.Vilchevskaya, Izvest. Akad. Nauk,

Div. Chem. Sci., 1949.

[35] A.N.Nesmeyanov, R.K.Freidlina, and A.E.Borisov, "Jubilee Symposium on the 30th Anniversary of the October Revolution," Izvest. Akad. Nauk, 1947, 658.

[36] A.N.Nesmeyanov and I.F.Lutsenko, Doklady Akad. Nauk, 59, 707 (1948).

[37] A.N.Nesmeyanov and A. K. Kochetkov, Izvest. Akad. Nauk, Div. Chem. Sci., 1949, 305.

[38] A.N.Nesmeyanov, V.A.Sazonova, and E.V.Landor, Doklady Akad. Nauk, 63, 395 (1948).

PHYSICO-CHEMICAL INVESTIGATION OF CONCENTRATED SOLUTIONS

X. THE $NaBr$-$AlBr_3$ AND KBr-$AlBr_3$ SYSTEMS IN THE MOLTEN STATE

E. Y. Gorenbein and E. E. Kriss

In our previous reports on our research into the conductivity, viscosity, and specific gravity of some molten systems of metal halides with $AlBr_3$ [1], we showed that when allowance is made for the viscosity, the curves of molar conductivity have an anomalous shape, and that the highest corrected molar conductivity is the conductance of the compounds that are formed in the given system. For example, in the $SbBr_3$ – $AlBr_3$ system the highest corrected conductivity is that of the coordination compound $SbBr_3 \cdot AlBr_3$, in the $ZnBr_2$ – $AlBr_3$ system that of the coordination compound $ZnBr_2 \cdot Al_2Br_6$, and in the $HgBr_2$ – $AlBr_3$ system that of the coordination compound $HgBr_2 \cdot Al_2Br_6$.

Our research on the NH_4Br – $AlBr_3$ system [2] showed that molar conductivity changes but very little with dilution, the curves of the corrected molar conductivity at different temperatures not being superimposed on one another, as is the case in other systems.

Naturally, it was of interest to examine how the corrected molar conductivity would change with dilution in analogous systems at different temperatures. To find out, we investigated the conductivity, viscosity, and specific gravity of the $NaBr$ – $AlBr_3$ and KBr – $AlBr_3$ systems at various concentrations and temperatures.

Initial Substances and Research Methods

Aluminum bromide was prepared as described in our previous reports, [1].

The sodium bromide was recrystallized several times, then dried, calcined, and stored in sealed ampoules.

The potassium bromide was repeatedly recrystallized, carefully dried, and then kept in a box in an exsiccator over P_2O_5.

The preparation of the solutions and the technique of measurement have been described in detail in a paper by one of the present authors [3].

We used a U-tube with well-ground stoppers, fitted with platinum electrodes, in measuring the conductivity. The electrodes were not platinized. The constants of the vessels we used ranged from 30 to 65; they were determined by means of an 0.1N solution of KCl. Operation of this type of container has been described in detail by Walden [4].

$NaBr$ – $AlBr_3$ System

The existence of two coordination compounds: $NaBr \cdot Al_2Br_6$ and $NaBr \cdot AlBr_3$ [5] in the $NaBr$ – $AlBr_3$ system was established by means of thermal analysis. Both

TABLE 3

NaBr – $AlBr_3$ System at t = 140°

NaBr % by weight	$x \cdot 10^3$	φ	μ	μ_1	$\eta \cdot 10^2$	d_4^t
1	2	3	4	5	6	7
11.15	45.68	334.8	15.29	88.2	9.29	2.756
12.10	50.00	307.3	15.36	92.5	9.69	2.767
14.41	64.14	252.8	16.21	100.1	9.94	2.787
15.29	68.67	241.3	16.56	105.4	10.25*	2.792
16.17	77.83	227.5	17.70	113.5	10.33	2.797

* The figure marked with an asterisk was found by interpolation.

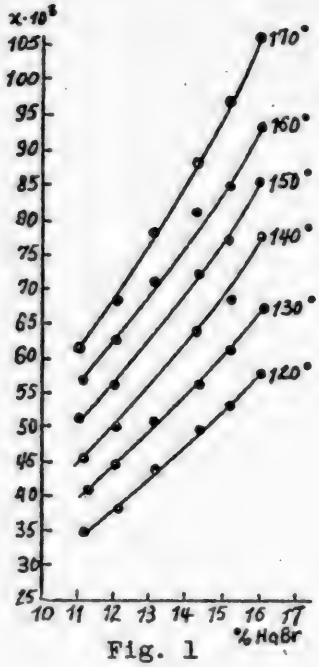


Fig. 1

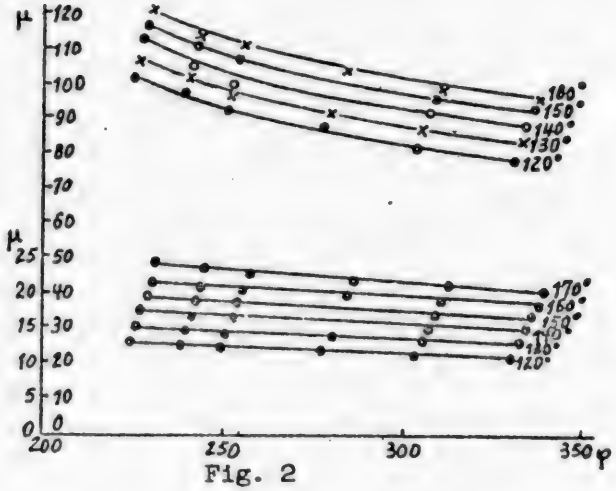


Fig. 2

The viscosity of pure $AlBr_3$ is given in the preceding paper [8].

The curves of Fig. 1 illustrate the variation of the specific conductivity of the NaBr – $AlBr_3$ system with the concentration of NaBr and with the temperature.

As is seen in the figure, the specific conductivity rises with rising temperature and concentration in the concentration range investigated by us.

Figure 2 shows the variation of the corrected and the uncorrected molar conductivity with dilution, the figures to the right of the axis of ordinates refer to the corrected molar conductivity.

As the curves of Fig. 2 indicate, the molar conductivity drops but little with increasing dilution, and when the viscosity corrections are introduced, the curves take on a clearly anomalous form, i.e., the corrected molar conductivity continues to fall, beginning with the individual molten electrolyte $NaBr \cdot Al_2Br_6$.

The curves of Fig. 3 show the variation of the viscosity of the NaBr – $AlBr_3$ system over the same range of concentrations and temperatures.

As the curves of Fig. 3 indicate, the viscosity rises with the increase in the concentration of NaBr, but drops as the temperature rises, the temperature coefficient of viscosity dropping considerably as the temperature is increased.

KBr – $AlBr_3$ System

The electrical conductivity of the KBr – $AlBr_3$ system was investigated by V.A.Izbekov and V.A.Plotnikov [7] at the temperature of 99.5°, and the viscosity by E.Y.Gorenbein [8] at the temperature of 100°.

We investigated this systemover the same concentration range as in the NaBr – $AlBr_3$ system, and were guided by the same considerations. It should be noted that thermal analysis indicates that the components of the KBr-$AlBr_3$ system form two compounds, $KBr \cdot Al_2Br_6$ and $KBr \cdot AlBr_3$ [5].

The highest concentration of components in this system examined by us corresponds to the formula $KBr \cdot Al_2Br_6$.

The results of measurement at 4 temperatures are listed in Tables 4-7 and are shown graphically for the entire temperature range investigated (110-170°). The tables are set up as those for the NaBr – $AlBr_3$ system.

The curves of Fig. 4 illustrate the variation of the viscosity of the KBr – $AlBr_3$ system with the concentration of KBr and with temperature. In this case, as in the preceding system, the viscosity rises with increasing KBr concentration and falls with rising temperature, the drop in viscosity becoming less rapid as the temperature increases.

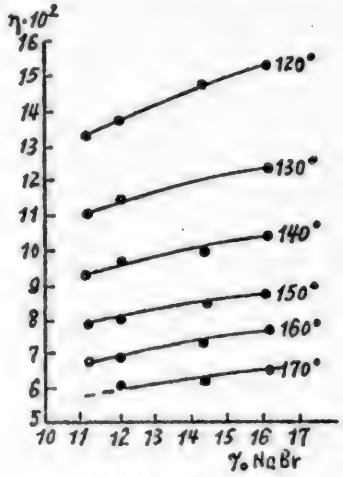


Fig. 3

Fig. 5 shows the variation of the specific conductivity with the KBr concentration. As is seen in the figure, the specific conductivity rises continuously with increasing KBr concentration and rising temperature.

TABLE 4

KBr – $AlBr_3$ System at t = 110°

KBr % by weight	$x \cdot 10^3$	φ	μ	μ_1	$\eta \cdot 10^2$	d_4^t
1	2	3	4	5	6	7
12.00	23.31	355.5	8.29	60.6	15.84	2.790
12.55	2 –	—	—	—	16.62	2.798
13.76	26.87	308.4	8.29	68.1	17.82	2.804*
15.28	30.09	277.2	8.34	72.9	18.96	2.810*
16.85	33.08	250.9	8.30	73.5	19.19	2.815
18.235	36.03	231.5	8.34	77.3	20.10*	2.818

* Figures marked with an asterisk were found by interpolation.

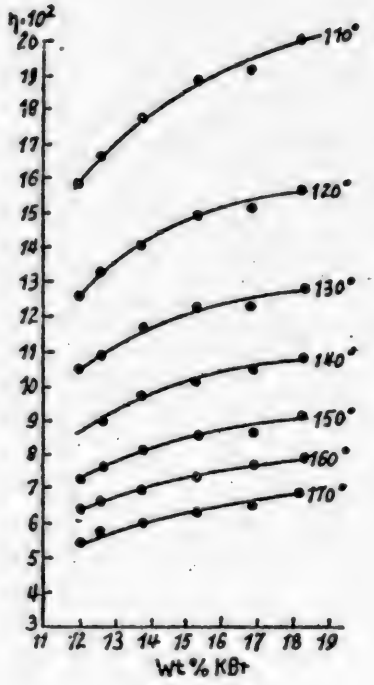


Fig. 4

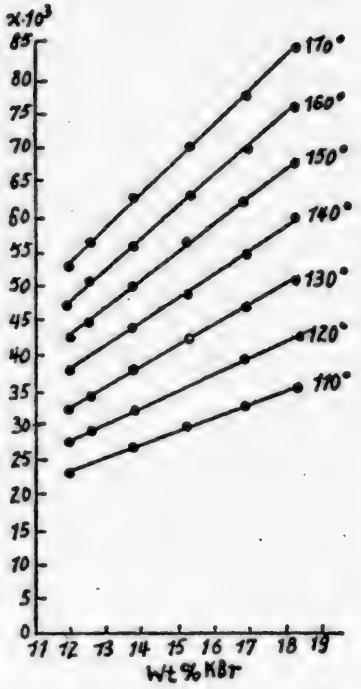


Fig. 5

The curves of Fig. 6 show the variation of the corrected and uncorrected molar conductivity with dilution. Here, as in the $NaBr-AlBr_3$ system, the molar conductivity slowly falls with dilution at the concentrations given in the table and rises with rising temperature. When the viscosity corrections are introduced, i.e., when the molar conductivity is based on the viscosity of the pure solvent, it takes on a clearly anomalous character – dropping noticeably with dilution.

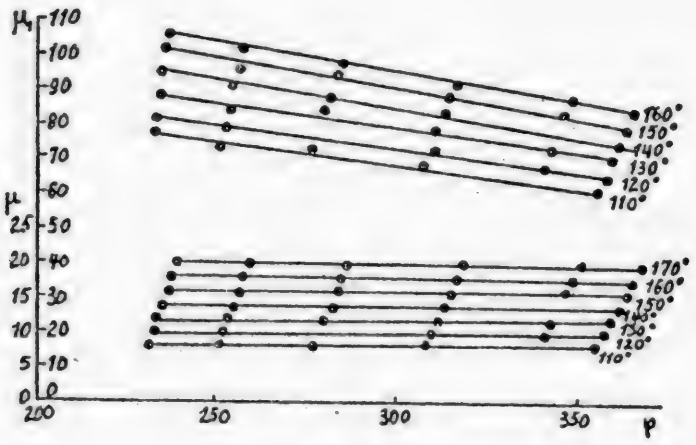


Fig. 6

TABLE 5

$KBr - AlBr_3$ System at t = 120°

KBr % by weight	$x \cdot 10^3$	φ	μ	μ_1	$\eta \cdot 10^2$	d_4^t
1	2	3	4	5	6	7
12.00	27.81	357.6	9.94	64.5	12.63	2.774
12.55	29.03	341.2	9.91	67.7	13.30	2.780
13.76	32.24	310.2	9.97	72.2	14.09	2.788*
15.28	–	–	–	–	14.97	2.794
16.85	39.82	252.2	10.04	78.4	15.20	2.804
18.235	43.15	232.9	10.05	81.2	15.73	2.802

* The figure marked with an asterisk was found by interpolation.

TABLE 6

$KBr - AlBr_3$ system at t = 130°

KBr % by weight	$x \cdot 10^3$	φ	μ	μ_1	$\eta \cdot 10^2$	d_4^t
1	2	3	4	5	6	7
12.00	32.43	359.8	11.67	69.5	10.49	2.757
12.55	34.53	343.1	11.85	73.1	10.87	2.764
13.76	37.82	312.0	11.80	78.8	11.76	2.772*
15.28	42.81	280.3	12.00	83.5	12.26	2.779
16.85	47.35	253.6	12.01	84.3	12.37	2.785
18.235	51.38	234.0	12.02	88.2	12.93	2.789

* The figure marked with an asterisk was found by interpolation.

TABLE 7

$KBr - AlBr_3$ system at t = 140°

KBr % by weight	$x \cdot 10^3$	φ	μ	μ_1	$\eta \cdot 10^2$	d_4^t
1	2	3	4	5	6	7
12.00	37.85	361.9	13.70	73.6	8.65	2.741
12.55	–	–	–	–	9.06	2.749
13.76	43.89	313.9	13.78	83.4	9.74	2.755
15.28	49.28	281.8	13.89	87.5	10.14	2.764
16.85	54.59	254.9	13.91	90.7	10.50	2.771
18.235	60.09	235.2	14.13	95.0	10.82	2.775

The fact that the isotherms of corrected conductivity do not lie close together in these two systems or in the $NH_4Br - AlBr_3$ system, but are spaced at considerable distances is worthy of note; it leads one to suppose that these systems are not binary and that their molar conductivity is a more complex function of the viscosity than that of inverse proportionality (for constant electrolytic dissociation, of course).

In our preceding investigations it was shown that the variation of corrected molar conductivity with dilution is satisfactorily expressed by the following equation for high concentrations, where the anomalies are found in the curves of the $\mu_1 - \varphi$ curves:

$$\mu_1 = \mu_o - k\frac{v - v_o}{v \cdot v_o}$$

where: μ_0 is the corrected molar conductivity of the individual electrolyte in the liquid state;

V_0 is the volume of a mole of this electrolyte, in liters;

V is the dilution, in liters;

μ_1 is the corrected molar conductivity for the given dilution;

k is a constant.

To check this function, we plotted the graph of $\mu_1 - \frac{V - V_0}{V \cdot V_0}$ for both systems at the same temperature of 120°. $\frac{V - V_0}{V \cdot V_0}$ was plotted along the abscissas axis, and μ_1 on the ordinates axis.

The numerical values of this function are listed in Tables 8 and 9.

TABLE 8

$NaBr - AlBr_3$ System at t = 120°

NaBr % by weight	μ_1	$\frac{V - V_0}{V \cdot V_0}$
11.15	78.6	1.424
12.10	81.8	1.143
13.18	88.6	0.836
14.41	93.3	0.444
15.29	98.9	0.257
16.17	102.3	0

TABLE 9

$KBr - AlBr_3$ System at t = 120°

KBr % by weight	μ_1	$\frac{V - V_0}{V \cdot V_0}$
12.00	64.5	1.497
12.55	67.7	1.363
13.76	72.2	1.070
16.85	78.4	0.329
18.235	81.2	0

As is shown by the curves of Fig. 7, as the dilution is increased, the corrected molar conductivity drops linearly, in full agreement with the foregoing equation.

The effect of dilution and temperature upon the product $\mu \cdot \eta$ yields the same result, as a rule, for strong electrolytes, but when we examine the effect of these same factors upon the corrected molar conductivity, i.e., the conductivity based upon the viscosity of the pure solvent, this effect is not always the same. Whereas $\mu \cdot \eta$ drops with rising temperature, μ_1, on the contrary, increases. We must make allowance here for change in the molecular state of the dielectric – the solvent – with rising temperature.

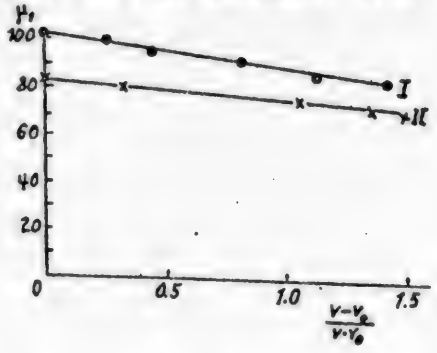


Fig. 7. I – NaBr-$AlBr_3$ at 120°
II – KBr–$AlBr_3$ at 120°.

This question is till moot owing to the absence of the necessary data on this relationship. Our explanation for the drop in the corrected molar conductivity is the same as was the case in our preceding reports [1,2,3,9], namely, that the condition of the electrolyte in the solution grows worse as dilution increases, i.e., the process of disintegration of the structural groups continues, with a shift to neutral ion pairs, which results in the anomalous form of the $\mu_1 - \varphi$ curves.

The fact that the conductivity of NaBr solutions in aluminum bromide as the solvent is much higher than that of KBr under the same conditions, which agrees completely with the increase in the atomic weight of the elements (Na and K), is quite interesting. This is illustrated in the curves of Fig. 8, in which there is plotted the variation of the corrected and uncorrected molar conductivity with dilution for both the NaBr – $AlBr_3$ and the KBr – $AlBr_3$ systems at 120°.

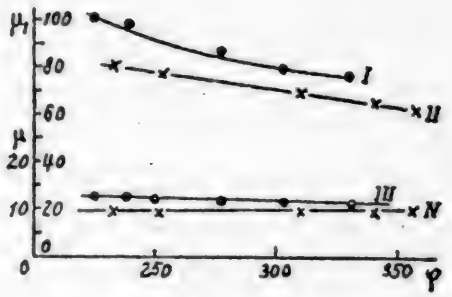


Fig. 8. $\left.\begin{matrix}\text{I}\\\text{III}\end{matrix}\right\}$ NaBr-$AlBr_3$ at 120°
$\left.\begin{matrix}\text{II}\\\text{IV}\end{matrix}\right\}$ KBr-$AlBr_3$ at 120°.

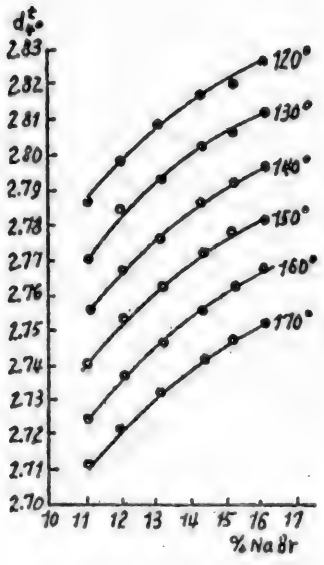


Fig. 9 .

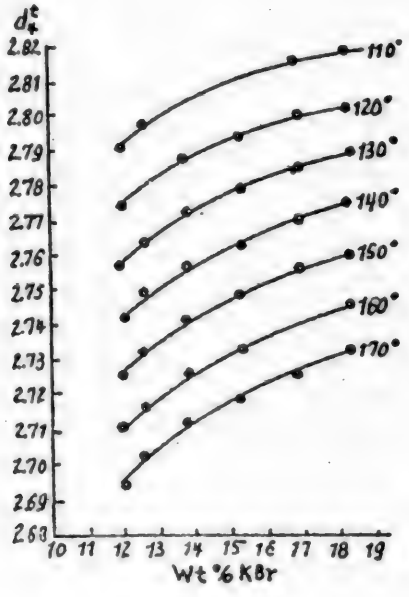


Fig. 10.

Specific Gravity

The specific gravity of solutions of NaBr and KBr in $AlBr_3$ as the solvent was determined as has been described in our preceding reports [2].

The results of measurement are listed in the last columns of Tables 1 - 7 and are shown graphically in Figs. 9 and 10, where the percentages by weight of the sodium and potassium bromide, respectively, are plotted on the abscissas' axis, and the specific gravity is plotted on the ordinates' axis. The curves of Fig. 9 show the specific gravity as a function of temperature and of the NaBr concentration for the NaBr – $AlBr_3$ system, the same function being shown in

Fig. 10 for the KBr – $AlBr_3$ system.

As is seen in the curves of Figs. 9 and 10, the specific gravity rises with increasing concentration of NaBr or KBr, but drops with rising temperature.

SUMMARY

1. The viscosity, conductivity, and specific gravity of NaBr – $AlBr_3$ and KBr – $AlBr_3$ systems in the molten state were investigated at various concentrations and temperatures.

2. It was found that the corrected molar conductivity of these systems is anomalous, its variation with dilution being satisfactorily expressed by the equation:

$$\mu_1 = \mu_0 - k \frac{V - V_0}{V \cdot V_0} .$$

3. It was found that the conductivity of solutions of NaBr in aluminum bromide as a solvent is much higher than that of KBr.

LITERATURE CITED

[1] E.Y.Gorenbein, J. Gen. Chem., 15, 729 (1945); 17, 873 (1947).

[2] E.Y.Gorenbein, J. Gen. Chem., 17, 873 (1947).

[3] E.Y.Gorenbein, Rep. Inst. Chem., Ukr. Acad. Sci., 7, 213 (1940); J. Gen Chem., 15, 729 (1945); 17, 873 (1947).

[4] P. Walden, H. Ulich and E.I.Birr, Z. phys Chem., 131, 1 (1927).

[5] J. Kendall, E.D.Crittenden and H. K. Miller, J. Am. Soc., 45, 963 (1923).

[6] E.Y.Gorenbein, J. Gen. Chem., 18, No. 8, (1948).

[7] V.A.Izbekov and V.A.Plotnikov, J. Russ. Phys. Chem. Soc., 43, 18 (1911).

[8] E.Y.Gorenbein, J. Gen. Chem., 15, 729 (1945).

Recieved May 17, 1948.

THE POLYTHERM OF THE $K_2Cr_2O_7$ — KBr — H_2O TERNARY SYSTEM

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In our research on the $K_2Cr_2O_7$ – KNO_3 – KCl – H_2O quaternary system [1] we established the appreciable drop of the individual solubility of the potassium bichromate in ternary and quaternary solutions of the foregoing system at low temperatures and at the optimum temperature. Potassium chloride possesses a particularly marked salting-out action upon potassium bichromate, the individual solubility of the potassium chloride being only negligibly lowered by the action of the potassium bichromate.

To compare the joint solubility of the salts in simple ternary aqueous systems that contain potassium as the common ion and potassium bichromate as the general component, we undertook an investigation of equilibria in the $K_2Cr_2O_7$ – KBr – H_2O system.

As far as we have been able to establish from the literature, the $K_2Cr_2O_7$ – KBr – H_2O system has not been fully investigated. We obtained the solubility polytherm of this system in the temperature range from 40° to complete solidification.

The material in the literature on the component binary systems $K_2Cr_2O_7$ – H_2O and KBr – H_2O is inadequate. The "composition – property (temperature)" diagram is plotted in fig. 1 for these binary systems to compare the individual solubilities of these salts. Most of the literature data on the $K_2Cr_2O_7$ – H_2O system has been taken from Karyakin [2], and for the KBr – H_2O from Mensser [3].

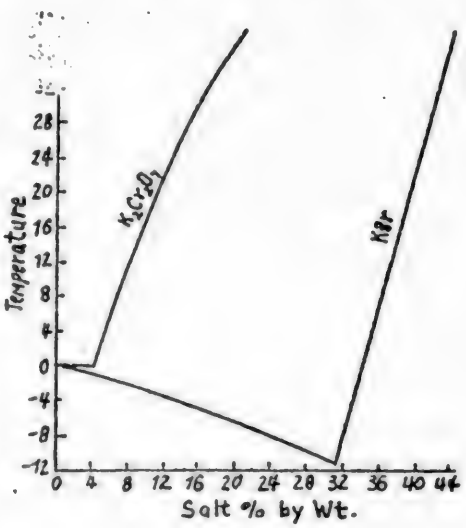

Fig. 1

Experimental checks of the points on the curves of these binary systems that were needed for our research indicated satisfactory agreement with the literature. All the data obtained by us for the first time for the foregoing systems fall on the crystallization lines for ice and the salts.

According to Koppel and Blumenthal [4], the crychydric point of the $K_2Cr_2O_7$ – H_2O system's curve is located at -0.6° and corresponds to 4.3%

of $K_2Cr_2O_7$. The cryohydric point of the curve of the KBr – H_2O system, as determined by Mensser [3], is at -1.15° and 31.2% of KBr.

The experimental data for the polytherm of $K_2Cr_2O_7$ – KBr – H_2O in the temperature range up to 20° were obtained by the visual-polythermal method. The joint solubility of the salts at 20, 30, and 40° were determined isothermally, in the usual water thermostat, with an accuracy of ±0.1°. The establishment of equilibrium was checked by analysis of samples of the liquid phase, taken every 2 hours. Equilibrium was usually established after 10-12 hours of continuous stirring. In the isothermal tests, the quantity of Br' and Cr_2O_7'' was determined by chemical analysis. These determinations served in the calculations to establish the percentages of the KBr and $K_2Cr_2O_7$ salts in the weighed samples of the liquid phase subjected to analysis. The Cr_2O_7 was determined iodometrically by titration by the Tsulkovsky method. The composition of the solid phase in equilibrium with the solution was determined for several points by the Schreinemakers method. Br' was determined by titration (Mohr

In the polythermal investigation we made 7 cuts along the KBr – H_2O edge toward the potassium bichromate. The results of measurement for these ternary sections are listed in summarized form in Table 1. The "composition – property" diagram for the first four sections is shown in Fig. 2.

The curves for the ternary cross sections, which resemble the curves of the $K_2Cr_2O_7$ – H_2O system in their general configuration, indicate fairly well both the negligible solubility of potassium bichromate in solutions of potassium bromide at low temperatures and the negligible depression of the melting point of the ice caused by the addition of potassium bichromate to solutions of potassium bromide. The ternary eutectic point of the $K_2Cr_2O_7$ – KBr – H_2O system, found by graphic interpolation of the experimental data obtained in the polythermal tests, is located at -11.7°, with the following composition of the liquid phase: 31.05% KBr, 0.2% $K_2Cr_2O_7$, and 68.75% H_2O.

Fig. 2

The isotherms of the $K_2Cr_2O_7$ – KBr – H_2O system were obtained for the following temperatures: 0, 10, 20, 30, and 40°. The 0 and 10° isotherms were plotted by graphical selection from the polythermal data of the ternary cross sections and the lateral binary systems. The isotherm data are listed in summarized form in Table 2. All the research data on the $K_2Cr_2O_7$ – KBr – H_2O system are generalized in the projection of the three dimensional diagram, the isotherm triangle of Fig. 3. The diagram does not show the isotherm curves for 0 and 10°, as they are too close to the polytherm line. The diagram of the $K_2Cr_2O_7$ – KBr – H_2O system has three crystallization areas: a large potassium bichromate area and small ice and potassium bromide areas.

We list below three systems investigated by us: $K_2Cr_2O_7$ – KNO_3 – H_2O, $K_2Cr_2O_7$ – KCl – H_2O, and $K_2Cr_2O_7$ – KBr – H_2O, to indicate the changes in the individual solubilities of the salts in ternary systems. These systems possess

TABLE 1

Point No.	Percent by weight			Molar per cent			Temperature	Solid phase
	H_2O	KBr	$K_2Cr_2O_7$	H_2O	KBr	$K_2Cr_2O_7$		
	Cross Section 1. (3% KBr + 97% H_2O) → $K_2Cr_2O_7$							
1	97	3.8	–	99.53	0.47	–	-0.7	ice
2	96.04	2.97	0.99	99.48	0.46	0.06	-0.8	ice
3	95.10	2.90	2.0	99.41	0.46	0.13	-1	ice + $K_2Cr_2O_7$
4	93.27	2.89	3.84	99.29	0.46	0.25	6.5	$K_2Cr_2O_7$
5	91.51	2.83	5.66	99.16	0.46	0.38	12.5	Ditto
6	89.81	2.78	7.41	99.04	0.46	0.50	17.5	–
	Cross Section 2 (5% KBr + 95% H_2O) → $K_2Cr_2O_7$							
1	95	5	–	99.21	0.79	–	-1.4	ice
2	94.37	4.97	0.66	99.17	0.79	0.04	-1.5	ice
3	93.85	4.95	1.20	99.13	0.79	0.08	-1.6	ice + $K_2Cr_2O_7$
4	92.53	4.87	2.60	99.04	0.79	0.17	4	$K_2Cr_2O_7$
5	90.77	4.77	4.46	98.91	0.79	0.30	11.5	Ditto
6	89.06	4.69	6.25	98.78	0.79	0.43	17.6	–
	Cross Section 3. (7% KBr + 93% H_2O) → $K_2Cr_2O_7$							
1.	93	7	–	98.88	1.12		-2.05	ice
2	92.39	6.95	0.66	98.84	1.12	0.04	-2.15	ice
3	92.07	6.93	1.0	98.82	1.13	0.05	-2.2	ice + $K_2Cr_2O_7$
4	90.88	6.84	2.28	98.72	1.13	0.15	6.2	$K_2Cr_2O_7$
5	89.42	6.73	3.85	98.61	1.13	0.26	12.5	ditto
6.	87.74	6.60	5.66	98.49	1.12	0.39	18.5	ditto
	Cross Section 4. (10% KBr + 90% H_2O) → $K_2Cr_2O_7$							
1.	90	10	–	98.35	1.65		-2.9	ice
2	89.56	9.95	0.49	98.32	1.65	0.03	-3.05	ice
3	89.47	9.93	0.6	98.31	1.65	0.04	-3.1	ice + $K_2Cr_2O_7$
4	88.24	9.80	1.96	98.24	1.65	0.11	8	$K_2Cr_2O_7$
5	87.38	9.71	2.91	98.15	1.65	0.20	13	ditto
6	86.53	9.62	3.85	98.08	1.65	0.27	17.5	ditto
	Cross Section 5 (15% KBr + 85% H_2O) → $K_2Cr_2O_7$							
1	85	15	–	97.40	2.60	–	-4.5	ice
2	84.57	14.93	0.50	97.36	2.61	0.03	-4.7	ice + $K_2Cr_2O_7$
3	84.16	14.85	0.99	97.33	2.60	0.07	4.5	$K_2Cr_2O_7$
4	83.33	14.71	1.96	97.26	2.60	0.14	14.5	ditto
5	82.93	14.63	2.44	97.23	2.60	0.17	17.2	ditto
	Cross Section 6. (20% KBr + 80% H_2O) → $K_2Cr_2O_7$							
1.	80	20	–	96.35	3.65	–	-6.5	ice
2	79.63	19.92	0.45	96.32	3.65	0.03	-6.7	ice + $K_2Cr_2O_7$
3	79.21	19.80	0.99	96.28	3.65	0.07	9.5	$K_2Cr_2O_7$
4	78.82	19.70	1.48	96.25	3.64	0.11	14.8	ditto
5.	78.43	19.61	1.96	96.21	3.64	0.15	19.1	ditto
	Cross Section 7. (25.86% KBr + 74.14% H_2O) → $K_2Cr_2O_7$							
1	74.14	25.86	–	95.00	5.00		-9	ice
2	73.91	25.78	0.31	94.96	5.02	0.02	-9.3	ice + $K_2Cr_2O_7$
3	73.76	25.73	0.51	94.95	5.01	0.04	5	$K_2Cr_2O_7$
4	73.00	25.47	1.53	94.87	5.01	0.13	20.5	ditto

TABLE 2

Point No	per cent by weight			Molar per cent			Solid phase
	H_2O	$K_2Cr_2O_7$	KBr	H_2O	$K_2Cr_2O_7$	KBr	
			Isotherm 0°				
1	99.57	4.43	–	99.72	0.28	–	$K_2Cr_2O_7$
2	94.90	2.20	2.90	99.40	0.14	0.46	$K_2Cr_2O_7$
3	91.90	1.20	6.90	98.80	0.08	1.12	$K_2Cr_2O_7$
4	84.40	0.70	14.90	97.35	0.05	2.60	$K_2Cr_2O_7$
5	73.84	0.40	25.76	94.96	0.03	5.01	$K_2Cr_2O_7$
6	65.40	0.30	34.30	92.63	0.02	7.35	$K_2Cr_2O_7$ + KBr
7	65.5	–	34.5	92.61	–	7.39	KBr
			Isotherm 10°				
1	92.50	7.50	–	99.51	0.49	–	$K_2Cr_2O_7$
2	92.25	4.90	2.85	99.21	0.32	0.47	$K_2Cr_2O_7$
3	90.02	3.20	6.78	98.66	0.22	1.12	$K_2Cr_2O_7$
4	83.80	1.40	14.80	97.30	0.10	2.60	$K_2Cr_2O_7$
5	79.18	1.00	19.82	96.28	0.07	3.65	$K_2Cr_2O_7$
6	61.6	0.50	37.90	91.44	0.04	8.52	$K_2Cr_2O_7$ + KBr
7	61.9	–	38.1	91.47	–	8.53	KBr
			Isotherm 20°				
1	88.90	11.10	–	99.24	0.76	–	$K_2Cr_2O_7$
2	87.98	8.06	3.96	98.77	0.55	0.68	$K_2Cr_2O_7$
3	85.55	4.53	9.92	97.96	0.32	1.72	$K_2Cr_2O_7$
4	80.49	2.55	16.96	96.73	0.19	3.08	$K_2Cr_2O_7$
5	75.97	1.93	22.1	95.64	0.15	4.21	$K_2Cr_2O_7$
6	68.00	1.19	30.81	93.49	0.10	6.41	$K_2Cr_2O_7$
7	64.37	0.88	34.75	92.37	0.08	7.55	$K_2Cr_2O_7$
8	60.20	0.65	39.15	90.98	0.06	8.96	$K_2Cr_2O_7$ + KBr
9	60.60	–	39.40	91.04	–	8.96	KBr
			Isotherm 30°				
1	84.60	15.40	–	98.90	1.10	–	$K_2Cr_2O_7$
2	83.64	10.32	6.04	98.19	0.74	1.07	$K_2Cr_2O_7$
3	78.53	4.94	16.53	96.55	0.37	3.08	$K_2Cr_2O_7$
4	70.97	2.56	26.47	94.46	0.21	5.33	$K_2Cr_2O_7$
5	64.11	1.56	34.33	92.37	0.14	7.49	$K_2Cr_2O_7$
6	58.11	0.95	40.94	90.28	0.09	9.63	$K_2Cr_2O_7$ + KBr
7	58.55	–	41.45	90.32	–	9.68	KBr
			Isotherm 40°				
1	79.40	20.60	–	98.44	1.56	–	$K_2Cr_2O_7$
2	78.58	14.58	6.84	97.61	1.11	1.28	$K_2Cr_2O_7$
3	74.07	7.23	18.70	95.77	0.57	3.66	$K_2Cr_2O_7$
4	72.29	4.21	23.50	94.99	0.34	4.67	$K_2Cr_2O_7$
5	55.93	1.65	42.42	89.56	0.16	10.28	$K_2Cr_2O_7$ + KBr
6	56.8	–	43.2	89.67	–	10.33	KBr

simple equilibrium diagrams, contain an identical cation, and a common component: potassium bichromate. The choice of systems makes it possible to use their comparison to indicate the mutual effects of salts with different anions upon the individual solubility of each salt in the respective ternary systems; in particular, it makes it possible to make a comparative evaluation of the effect of salts with different anions upon the change in the individual solubility of the component that is common to all the ternary systems.

In order to compare the individual and joint solubility of the salts making up the solutions, we express the individual particles – ions and molecules – present in the solution as mol fractions, basing our approach on the assumption that strong electrolytes are practically fully dissociated in aqueous solutions of any concentration, and that systems possessing simple equilibrium diagrams cannot form stable complex ions in aqueous solutions.

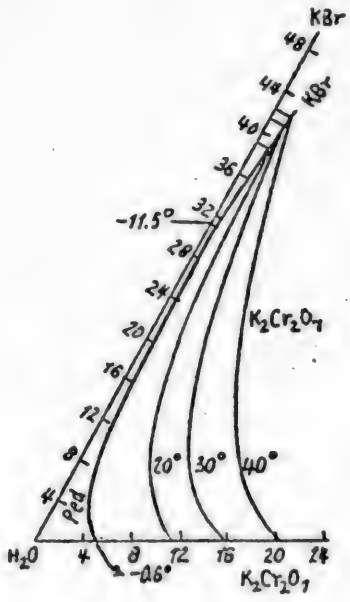

Fig. 3

The mol fraction is found from the equation:

$$N_i = \frac{n_i}{n_i + \sum n_j},$$

where n_i = the number of moles of the given individual particles; and n_j = the number of moles of all the other individual particles. In the ternary system we have selected for comparison, the anions are the unshared ions. We therefore take the ratio of the mol fraction of the anion in a saturated solution of the binary aqueous system to the mol fraction of the same anion in a eutonic solution of the respective ternary system as a measure of the change of the individual solubility of the salt in ternary solutions at the given temperature.

For instance: the change in the individual solubility of the salts in the $K_2Cr_2O_7 - KCl - H_2O$ system at the given temperature will be given by the ratio $\frac{N_{Cr_2O_7''\ indiv.}}{N_{Cr_2O_7''\ joint}}$ for potassium bichromate, and by $\frac{N_{Cl'\ indiv.}}{N_{Cl'\ joint}}$ for potassium chloride, where $N_{Cr_2O_7''\ indiv.}$ and $N_{Cl'\ indiv.}$ are the mol fractions of the anions in the saturated solution for the individual solubility of the salts, and $N_{Cr_2O_7''\ joint}$ and $N_{Cl'\ joint}$ are the mol fractions of the anions in the solution saturated with both salts for the joint solubility of these salts.

It is obvious that this ratio expresses the maximum change in the individual solubility of a salt in a ternary solution, besides underscoring the special nature of the effect of salts with different anions upon the component that is common to the systems under comparison.

Table 3

Temperature	$K_2Cr_2O_7 - KNO_3 - H_2O$				$K_2Cr_2O_7 - KCl - H_2O$				$K_2Cr_2O_7 - KBr - H_2O$			
	g per 100 g of saturated solution		$N_{Cr_2O_7}''$ indiv.	$N_{NO'}$ indiv	g per 100 g of saturated solution		$N_{Cr_2O_7}''$ indiv	$N_{Cl'}$ indiv	g per 100 g of saturated solution		$N_{Cr_2O_7}''$ indiv	$N_{Br'}$ indiv
	$K_2Cr_2O_7$	KNO_3	$N_{Cr_2O_7}''$ joint	$N_{NO'}$ joint	$K_2Cr_2O_7$	KCl	$N_{Cr_2O_7}''$ joint	$N_{Cl'}$ joint	$K_2Cr_2O_7$	KBr	$N_{Cr_2O_7}''$ joint	$N_{Br'}$ joint
0°	4.43	0.0			4.43	0.0			4.43	0.0		
	0.0	11.5			0.0	21.9			0.0	34.5		
	1.68	11.56	2.50	0.98	0.34	21.4	12.02	1.02	0.3	34.3	11.65	1.00
10°	7.5	0.0			7.5	0.0			7.5	0.0		
	0.0	17.7			0.0	23.8			0.0	38.1		
	2.70	16.60	2.62	1.06	0.45	23.4	15.61	1.02	0.5	37.9	11.74	1.00
20°	11.1	0.0			11.1	0.0			11.1	0.0		
	0.0	24.1			0.0	25.5			0.0	39.4		
	4.61	22.54	2.17	1.03	0.90	25.40	11.76	0.99	0.65	39.15	13.65	1.00
30°									15.40	0.0		
									0.0	41.45		
									0.95	40.94	13.24	1.01
40°	20.6	0.0			20.6	0.0			20.6	0.0		
	0.0	39.1			0.0	28.7			0.0	43.2		
	8.65	35.17	2.55	1.30	2.28	27.25	9.25	1.04	1.65	42.42	10.51	1.01

Governed by the foregoing considerations, we give in Table 3 a summary of the data showing the change in the individual solubility of salts in the ternary systems mentioned above.

The figures in Table 3 indicate that the concentrations of the elementary anions Cl' and Br' undergo almost no change at various temperatures in eutonic ternary solutions of the corresponding systems with respect to concentration in the saturated solution for an individual solubility of the salts, whereas the concentration of the complex anion Cr_2O_7'', which is present in the same eutonic solution drops appreciably. The same drop in the concentration of the Cr_2O_7'' anion occurs, though on a smaller scale, when it is part of a ternary solution with the NO_3' anion.

Apparently, the structural peculiarities of anions affect the crystallization of salts from ternary solutions.

SUMMARY

1. Joint solubility was investigated by the methods of physico-chemical analysis in the $K_2Cr_2O_7 - KBr - H_2O$ system from + 40° to total solidification of the solution.

2. The system diagram has three crystallization areas: ice, potassium bichromate, and potassium bromide.

3. The individual solubility of potassium bichromate drops appreciably in ternary solutions of the $K_2Cr_2O_7 - KBr - H_2O$ system.

4. The salting-out effect with respect to potassium bichromate is arranged in increasing value in the following salt series: $KNO_3 - KCl - KBr$.

LITERATURE CITED

[1] A.P.Palkin and P.S.Bogoyavlensky, J. Appl. Chem., No. 6 (1941).

[2] Y.V.Karyakin. Pure Chemical Reagents. State Chemical Publishers, 1947.

[3] A. Mensser, Z. allg. anorg. Ch., 44, 80 (1905).

[4] Koppel and Blumenthal, Z. allg. anorg Ch., 53 (1906).

Received May 17, 1948

RESEARCH ON THE STRUCTURAL DIAGRAM OF THE Al-Cu-Mg-Si SYSTEM

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1. Survey of the Literature on Research Into This System

a) Ternary Systems

The Al – Cu – Mg System

In recent time, the Al-Cu-Mg system has been independently investigated by thermal and microscopic methods by G.G.Urazov and D.A.Petrov [1] in the N.S.Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and Nishimura [2] in Japan. The diagram plotted by G.G.Urazov and D.A.Petrov is shown in Fig. 1.

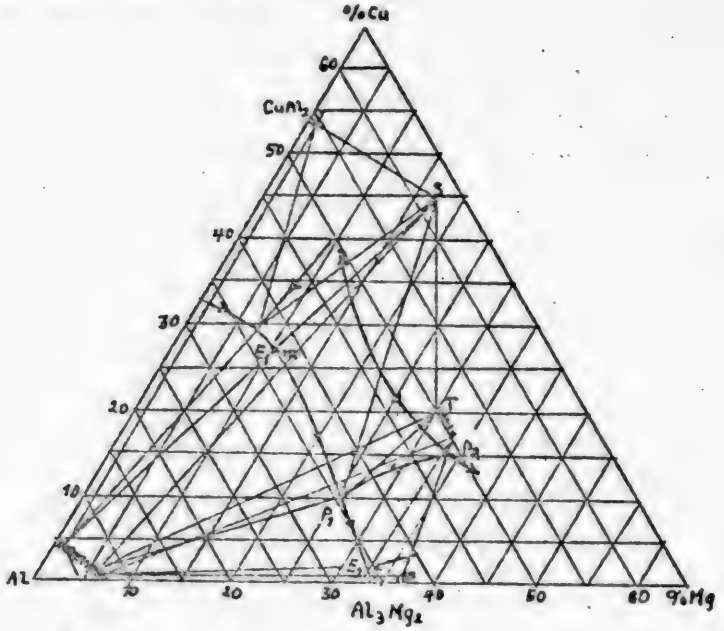

Fig. 1. Structural Diagram Al-Cu-Mg (Urazov, Petrov)

Contradicting Vogel [3], who found only one ternary phase, Al_6CuMg_4, in the Al - Cu - Mg system, and Janecke [4], who arbitrarily assumed that the ternary phase found by Vogel was a solid solution based on Al_3Mg_2, i.e., totally rejected the presence of ternary phases in the system, Urazov, Petrov, and Nishimura established the existence of two ternary phases, denoted by the symbols S and T. The authors' diagrams are of the same type, differing only in their indications of the phase compositions and of the nonvariant points.

In accordance with these diagrams, the aluminum vertex of the Al - Cu - Mg system is divided into 3 secondary systems:

1) Al - $CuAl_2$ - S with a nonvariant eutectic point: liq. $\rightleftharpoons$ Al + $CuAl_2$ + + S at 501°, corresponding to a composition of 63.1% Al, 29.7% Cu, and 7.2% Mg (according to Urazov and Petrov) or 64% Al, 26.8% Cu and 6.2% Mg (according to Nishimura).

2) Al - S - T with the nonvariant eutectic point: liq. + S $\rightleftharpoons$ T + Al at 465°, corresponding to a composition of 64.4% Al, 10.0% Cu and 25.6% Mg (according to Urazov and Petrov) or 64% Al, 11% Cu and 25% Mg (according to Nishimura).

3) Al + T + Al_3Mg_2 with the nonvariant eutectic point: liq. $\rightleftharpoons$ Al + T + + Al_3Mg_2 at 445°, corresponding to a composition of 65.5% Al, 1.5% Cu and 33.0% Mg (according to Urazov and Petrov) or 65% Al, 3% Cu and 32% Mg (according to Nishimura).

Al – Cu – Si System

The Al - Cu - Si system has been investigated by Fuss [5], Gwyer, Phillips, and Mann [6], and G.G.Urazov, S.A.Pogodin, and Zamoruyev [7]. The same type of Al - Cu - Si structural diagram was plotted in all three research papers as far as the aluminum vertex is concerned. The system is a ternary eutectic mixture of Al, $CuAl_2$, and Si phases. The nonvariant eutectic point was found to lie at 525°, corresponding to the following composition: 65.8% Al, 29.0% Cu and 5.2% Si (according to Fuss); 67.5% Al, 26% Cu and 6.5% Si (according to Gwyer, Phillips, and Mann); and 63.5% Al, 31.5% Cu and 5% Si (according to Urazov, Pogodin, and Zamoruyev).

Al – Mg – Si System

The Al - Mg - Si System has been investigated by Hanson and Gayler [8]. According to their diagram, the aluminum vertex of the system consists of two secondary systems:

1) Al – Al_3Mg_2 – Mg_2Si, with the nonvariant eutectic point: liq $\rightleftharpoons$ Al + + Al_3Mg_2 + Mg_2Si at 448°, corresponding to a composition of 65.25% Al, 34.0% Mg and 0.75% Si.

2) Al – Mg_2Si – Si, with the nonvariant eutectic point: liq. $\rightleftharpoons$ Al + + Mg_2Si + Si at 550°. The composition of the liquid and of the nonvariant point were not determined.

b) The Al – Cu – Mg – Si Quaternary System

We know of only two papers, by Gayler and by Dix and associates, that have any bearing on our research problem.

Gayler [9] investigated alloys at the aluminum vertex of the Al - Cu - Mg - Si quaternary system, up to 6% Cu, 4% Mg, and 4% $MgSi_2$, along the two sectional

planes Al - Mg_2Si - Cu:Mg (3:1) and Al - Mg_2Si - Cu:Mg (2:3); on the basis of his results, he stated the phase boundaries in the solid state for two temperatures, 400° and 250°.

Both of Gayler's isothermal cross sections cover the following regions: 1) the monophase region of an α-solid solution; 2) two diphase regions, α + +$CuAl_2$ and α + Mg_2Si; and 3) a triphase region α + Mg_2Si + $CuAl_2$.

Gayler did not know of the existence of the ternary phase S in the Al - Cu - Mg system, discovered in 1936 by Laves and Witte [10] (cf also [1,2] and apparently disregarded the presence of another ternary phase T in this system, which had been discovered by Vogel in 1919.

Moreover, his cross sections, as we shall see later when we discuss the system on p a475, run as follows: one (Cu:Mg = 3:1) through the tetrahedron Al - $CuAl_2$ - S - Mg_2Si and the other (Cu:Mg = 2:3) through the tetrahedron Al - S - T - Mg_2Si. Correspondingly, the alloys he did research on should possess the following phases: alpha solution, $CuAl_2$, Mg_2Si, and S along the Cu:Mg = 3:1 cross section, and alpha solution, Mg_2Si, S and T along the Cu:Mg = 2:3 cross section.

Hence, Gayler did not notice the S phase in the alloys of the first cross section and evidently took this phase to be $CuAl_2$ in the alloys of the second cross section, failing to notice phase T. Apart from the presence of ternary phases, the four-phase region, which is missing in Gayler's paper, should have occupied the corresponding position along the cross sections of the quaternary system investigated by Gayler.

All this compelled us to consider the results reported by Gayler as not reflecting the actual relationships in the alloys on which he had done research and to ignore them in our further consideration of the system.

Dix, Sager, and Sager [11] investigated some alloys at the aluminum vertex of the Al - Cu - Mg - Si system, prepared from the purest aluminum. They added the Mg and Si in proportions calculated to form the compound Mg_2Si. In fact, Si was present in an excess of from 0.03 to 0.16% in all their alloys (with a constant calculated percentage of 1.3% Mg_2Si).

In all their alloys the authors found, in addition to α, Cu Al_2, and Mg_2Si, a fourth structure which they believed ought to contain all four components of the system they were investigating, i.e., Al, Cu, Mg, and Si, and thus was the quaternary phase.

The authors indicate that this phase is easily distinguishable from Mg_2Si under the microscope, but that it could be confused with $CuAl_2$. Both phases, $CuAl_2$ and Al - Cu - Mg - Si, are gray in color in a neutral polish section, according to their descriptions, the quaternary phase appearing to be somewhat darker. When etched with hot 10% HNO_3, the $CuAl_2$ turns brown, whereas the Al - Cu - Mg - Si turns blue at first, becoming thoroughly pitted with further etching. When etched with hot NaOH, $CuAl_2$ turns brown in 4 seconds, whereas Al - Cu - Mg - Si is outlined; a 0.5% solution of HF outlines both the $CuAl_2$ and the Al - Cu - Mg - Si.

The authors also established the solidus temperature as 510.5° for Alloy 4541 (with 4.82% Cu, 0.58% Si, and 0.83% Mg).

Lastly, in Alloy M7436, with 2.80% Cu, 0.85% Mg, and 1.06% Si, they found free silicon, in addition to $CuAl_2$ and Al - Cu - Mg - Si, but found no Mg_2Si, pointing out in this connection that at certain concentrations the quaternary phase is evidently more stable than Mg_2Si.

Using the results reported by Dix, Sager, and Sager, Petrov [12] indicated the supposed limits of the atomic ratios of these elements in the quaternary phase and proposed the formula $Al_xCu_4Mg_5Si_4$ for the phase. These figures were used by us in our investigation of the structural diagram.

2. Description of Experimental Methods

Research on the structural diagrams was effected by plotting the cooling curves with the pyrometer designed by Academician N.S. Kurnakov and by studying the microstructure of the alloys along certain cross sections.

The constituents used in preparing the alloys were: aluminum containing 0.17% Si and 0.17% Fe; magnesium containing 0.06% Al and 0.10% Fe; electrolytic copper; and silicon containing 0.26% Al and 0.87% Fe. As a rule, in studying the cross sections, we first prepared a sufficient quantity of the two extreme (ternary) alloys for each cross section. Smelting was done in graphite crubibles in cryptolite furnaces, oxidation of the metal being prevented by first fusing in the crucible an adequate amount of flux, consisting of a mixture of potassium chloride and magnesium chloride in equimolecular proportions (carnallite), which had been previously desiccated with care to eliminate the water of crystallization from the magnesium chloride and then fused.

The aluminum was added to the liquid salt bath in the crucible, followed by the melt: copper and silicon, or copper and magnesium, or silicon and magnesium, depending on the alloy to be prepared.

During the smelting process, more flux was added to the crucible as needed so that the metal was always covered by a protective layer of fused salts. To prevent the metal from entrapping flux during pouring, a small quantity of ammonium fluoride was sprinkled over the surface of the bath before pouring (but after careful stirring of the melt) in order to form a solid coating over the surface of the metal. Then the alloy was poured into a cold metal mold, forming a round ingot 16 mm in diameter that solidified almost instantaneously, thus preventing the formation of an alloy with nonhomogeneous composition. Besides, ingots of this size could be easily pulverized for weighing.

The alloys were usually preheated under carnallite in graphite crucibles placed in cryptolite furnaces before recording their cooling curves. Sometimes, when we expected the critical points on the cooling curve to be close to the freezing point of carnallite (460-490°) we used a flux with a lower melting point: 54.5% by weight of KCl and 45.5% by weight of LiCl, which melted at a temperature below the melting point of zinc.

The weighed batches (averaging 60 g) were made up of ready ternary alloys. After the alloy had been heated up enough, and the melt had been carefully stirred, the furnace circuit was disconnected, and the hot junction of a Pt-PtRh thermocouple made up of 0.5 mm wires was introduced into the metal. The ends of the thermocouple, insulated from each other in a two-duct porcelain tube, were protected against the metal by a porcelain cap.

The cold junction of the thermocouple was always kept at 0° in melting ice. The thermocouple was dipped into the metal so that the hot junction was 8 to 10 mm from the bottom of the crucible and was on the latter's longitudinal axis. The crucible was covered with an asbestos or fireclay cover. Cooling took 40 to 70 minutes, depending on the nature of the alloy and the initial cooling temperature.

The loss in preparing the alloys was not high, of the order of tenths of one per cent.

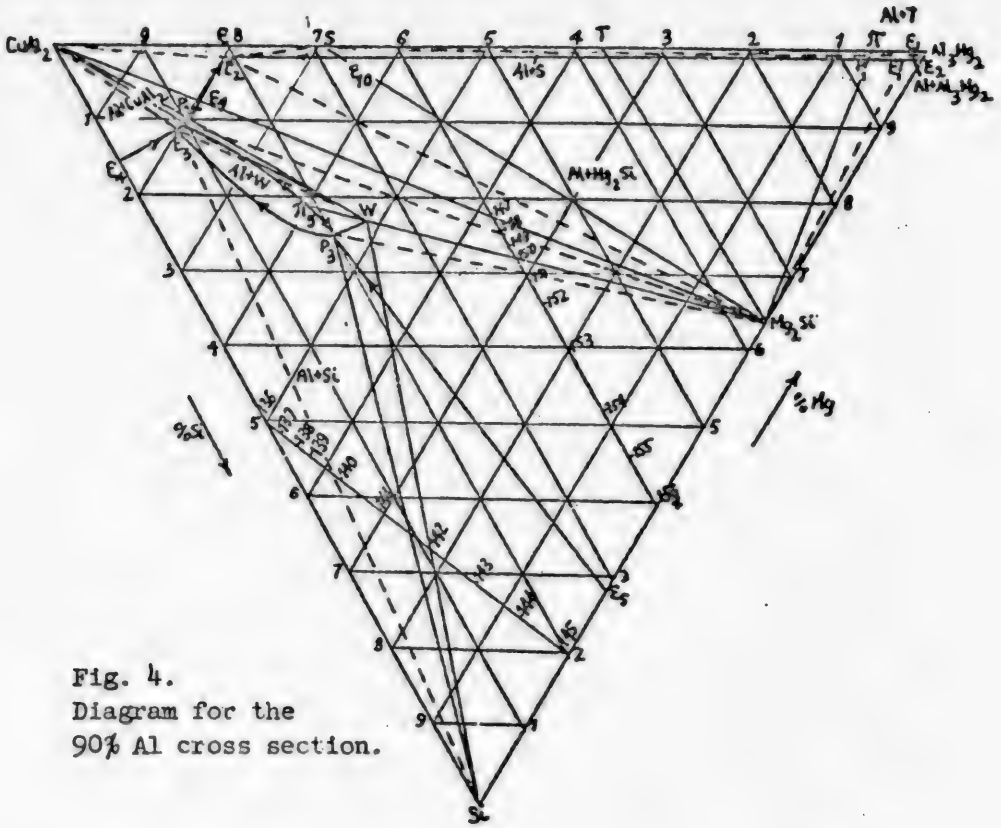

Fig. 4.
Diagram for the
90% Al cross section.

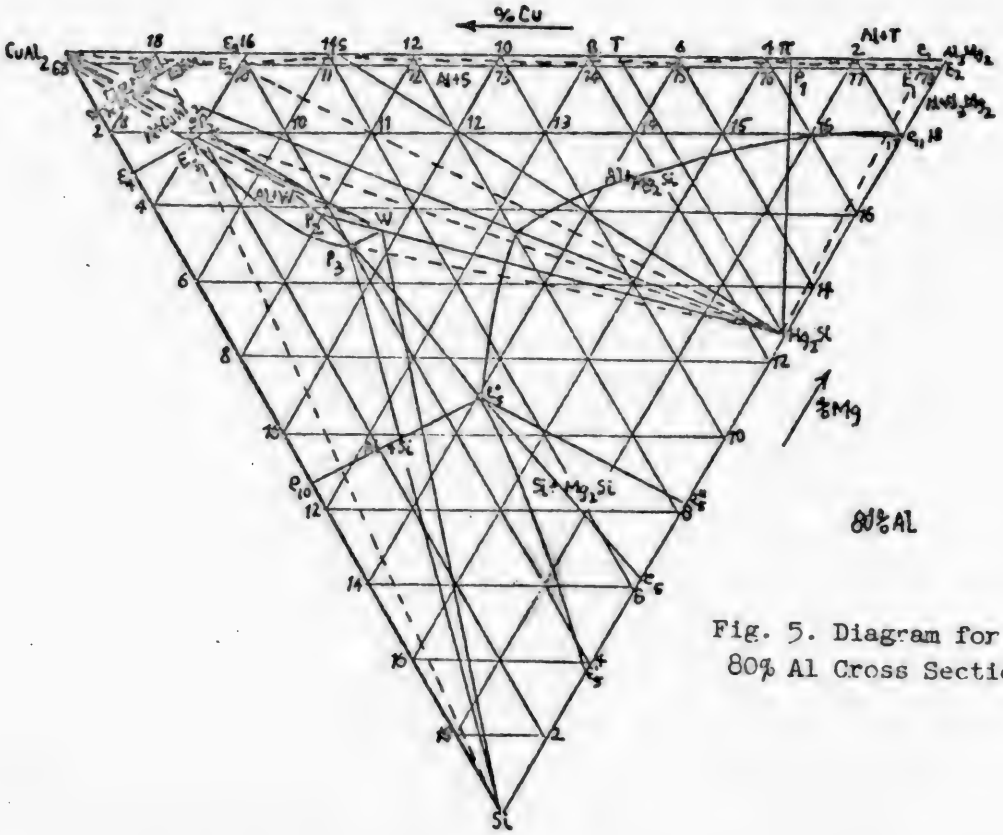

Fig. 5. Diagram for the
80% Al Cross Section

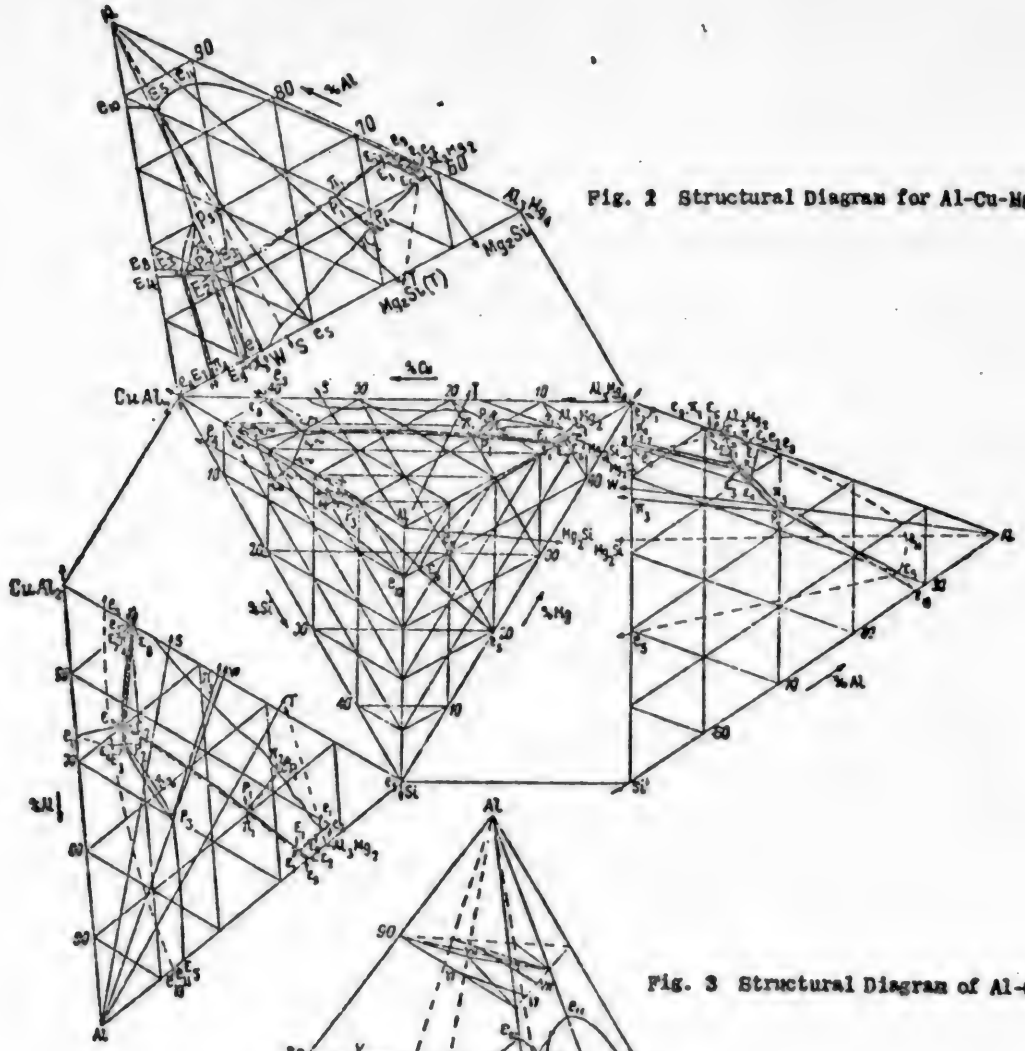

Fig. 2 Structural Diagram for Al-Cu-Mg-Si

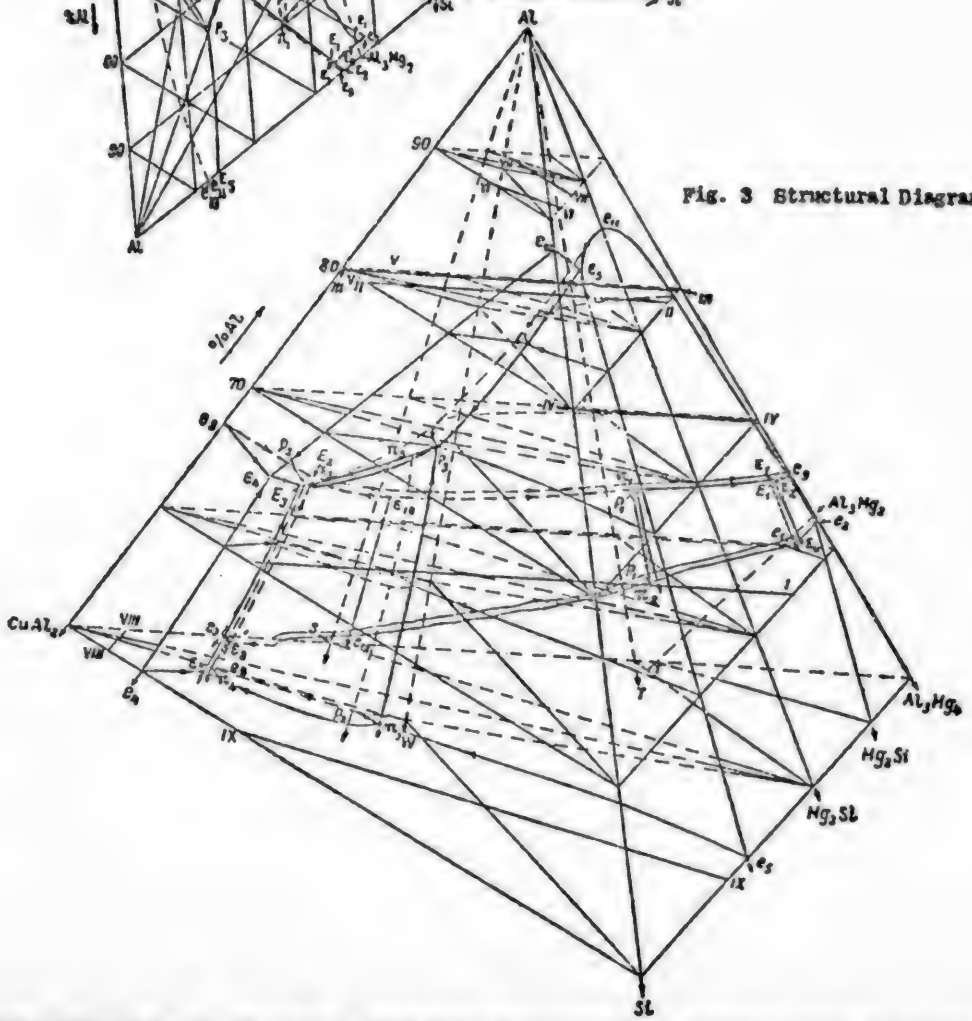

Fig. 3 Structural Diagram of Al-Cu-Mg-Si

3. Al – Cu – Mg – Si Structural Diagram

In Fig. 2 there is plotted part of the structural diagram of Al - Cu - Mg - Si investigated by us down to 50% Al, in four projections: a horizontal projection on the 50% Al plane parallel to the Cu - Mg - Si base of the tetrahedron, and three vertical projections that are perpendicular to the three sides of the horizontal projection.* In Fig. 3 the structural diagram is shown in perspective, showing the location of the I - II, II - II,....IX - IX cross sections explored in plotting the diagram.

The diagrams for the plane cross sections of the Al - Cu - Mg - Si tetrahedron are given in Figs. 4-8 for 90, 80, 70, 60, and 50% Al, and the diagrams of the investigated linear cross sections are shown in Figs. 9 - 17.

The phase compositions and the locations of the nonvariant points in the ternary systems were taken, with some corrections, from the corresponding diagrams in the papers of G.G.Urazov and D.A.Petrov [1], G.G.Urazov, S.A. Pogodin, and G.M.Zamoruyev [7], and Hanson and Gayler [8]. The corrections were based on the results of our investigation of the Al - Cu - Mg - Si system.

According to our data, the nonvariant point in the Al - Mg - Si system corresponding to the equilibrium liq. $\rightleftharpoons$ Al + Mg_2Si + Al_3Mg_2, is much closer to the Al - Mg edge than is stated by Gayler. It is close to the following composition: 0.3% Si, 34.6% Mg, 65.1% Al. The position of the other nonvariant point in the same system, corresponding to the equilibrium: liq. $\rightleftharpoons$ Al + + Si + Mg_2Si, was found to be about 10% Si., 3.9% mg, and 86.1% Al. The position of the nonvariant point in the Al - Cu - Si system is closest to the composition of 5.2% Si, 29.0% Cu, 65.8% Al, given by Fuss [5].

We were able to establish the composition of the quaternary phase W from the results of a merely approximate thermal analysis. The Cu:Mg:Si = 4:5:4 ratios, in atomic percentages, previously established by us, [12], have been confirmed by the present research. The percentage of aluminum in W is between 30 and 40%. It was assumed to be 30% when we constructed the structural diagram. In accordance with the structural diagrams (Figs. 2 and 3), the Al participates in six nonvariant equilibria, three of which are eutectic:

1) Liq. $\rightleftharpoons$ Al + $CuAl_2$ + Si + Mg_2Si at the point E_3,

2) Liq. $\rightleftharpoons$ Al + $CuAl_2$ + S + Mg_2Si at the point E_2,

3) Liq. $\rightleftharpoons$ Al + T + Al_3Mg_2 + Mg_2Si at the point E_1,

and three are peritectic:

4) Liq. + Mg_2Si $\rightleftharpoons$ Al + Si + W at the point P_3,

5) Liq. + Mg_2Si $\rightleftharpoons$ Al + $CuAl_2$ + W at the point P_2,

6) Liq. + S $\rightleftharpoons$ Al + Mg_2Si + T at the point P_1.

The compositions and temperatures corresponding to the nonvariant points are listed in Table 1.

The three nonvariant points E_2, P_1 and E_1 have compositions and temperatures that are close to those of the corresponding nonvariant points $\varepsilon_3\pi_1\varepsilon_1$ (Fig. 3) in the Al - Cu - Mg ternary system (points E_2, P_1, and E_1 in Fig. 1). They lie close to the Al-Cu - Mg side of the tetrahedron, along which the most easily fusible phases of the system are located. The three other nonvariant points are also shifted toward the Al - Cu - Mg side, on the whole.

The surfaces of secondary crystallization are the boundaries of seven spaces of primary crystallization of the phases: Al, Si, $CuAl_2$, Mg_2Si, W, S,

* The justification for representing a quaternary system by such a method and the theory of quaternary systems, elaborated by us and employed in the present paper, will be found in our research paper [13].

T, and Al_3Mg_2 in the tetrahedron (Fig. 3).

TABLE 1

List of Nonvariant Points at the Aluminum Vertex of the Tetrahedron

Nonvariant point	Equilibrium	Position of nonvariant point				
		Composition (% by weight)				Temp. °C
		Al	Cu	Mg	Si	
E_3	Liq. $\rightleftharpoons$ Al + $CuAl_2$ + Si + Mg_2Si	64.8	28.3	3.1	4.0	505
E_2	Liq. $\rightleftharpoons$ Al + $CuAl_2$ + S + Mg_2Si	62.8	29.6	7.15	0.45	500
E_1	Liq. $\rightleftharpoons$ Al + T + Al_3Mg_2 + Mg_2Si	65.3	1.5	32.9	0.3	444
P_3	Liq. + Mg_2Si $\rightleftharpoons$ Al + Si + W	70.0	16.5	6.0	7.5	521
P_2	Liq. + Mg_2Si $\rightleftharpoons$ Al + $CuAl_2$ + W	64.4	28.3	3.6	3.7	510*
P_1	Liq. + S $\rightleftharpoons$ Al + Mg_2Si + T	64.2	10.0	25.5	0.3	505

*This temperature is close to the solidus temperature of the alloy (510.5°) given by Dix and associates (cf. p. a 472) for 4.82% Cu, 0.48% Si and 0.83% Mg, this position being within the Al-Mg_2Si-$CuAl_2$-W tetrahedron.

The locations of the surfaces of secondary crystallization and the lines of tertiary crystallization in the tetrahedron are described in Table 2.

TABLE 2

Surfaces and Lines of Crystallization in the Al – Cu – Mg – Si Concentration Tetrahedron

Equilibrium	Crystallization Surfaces and Lines
I. Surfaces of Secondary Crystallization	
1. Liq. $\rightleftharpoons$ Al + Si	$e_{10}\varepsilon_5P_3E_3\varepsilon_4e_{10}$
2. Liq. $\rightleftharpoons$ Al + $CuAl_2$.....	$e_8\varepsilon_4E_3P_2\varepsilon_9E_2\varepsilon_3e_8$
3. Liq. $\rightleftharpoons$ Al + W	$P_3E_3P_2\pi_5P_3$
4. Liq. $\rightleftharpoons$ Si + $CuAl_2$.....	$e_4\varepsilon_4E_3\varepsilon_7e_4$
5. Liq. $\rightleftharpoons$ Si + W	$P_3E_3\varepsilon_7\pi_3P_3$
6. Liq. $\rightleftharpoons$ $CuAl_2$ + W	$E_3P_2\pi_4\varepsilon_7E_3$
7. Liq. $\rightleftharpoons$ Al + Mg_2Si.....	$e_{11}\varepsilon_2E_1P_1E_2\varepsilon_8P_2\pi_5P_3\varepsilon_5e_{11}$
8. Liq. $\rightleftharpoons$ Si + Mg_2Si.....	$e_5\pi_3P_3\varepsilon_5e_5$
9. Liq. + Mg_2Si $\rightleftharpoons$ W	$\pi_3P_2\pi_4P_2\pi_5P_3\pi_3$ with maximum temperatures at the line $p_2\pi_5$
10. Liq $\rightleftharpoons$ $CuAl_2$ + Mg_2Si	$\pi_4e_8\varepsilon_8E_2\varepsilon_9P_2\pi_4$ with maximum temperatures at the line $e_8\varepsilon_9$
11. Liq. $\rightleftharpoons$ Al + S	$\varepsilon_3E_2\varepsilon_{10}P_1\pi_1\varepsilon_3$ with maximum temperatures at the line $e_{13}\varepsilon_{10}$
12. Liq. $\rightleftharpoons$ $CuAl_2$ + S	$e_3\varepsilon_8E_2\varepsilon_3e_3$
13. Liq. $\rightleftharpoons$ Mg_2Si + S	$\varepsilon_8e_{12}\pi_2P_1\varepsilon_{10}E_2\varepsilon_8$ with maximum temperatures at the line $e_{12}\varepsilon_{10}$.
14. Liq. $\rightleftharpoons$ Al + T	$\pi_1P_1E_1\varepsilon_1\pi_1$
15. Liq. + S $\rightleftharpoons$ T	$\pi_1P_1\pi_2p_1\pi_1$

Table 2 continued

Equilibrium	Crystallization Surfaces and Lines
16. Liq. $\rightleftharpoons Mg_2Si + T$	$P_1E_1\varepsilon_8\pi_2P_1$
17. Liq. $\rightleftharpoons Al + Al_3Mg_2$	$e_9\varepsilon_1E_1\varepsilon_2e_9$
18. Liq. $\rightleftharpoons T + Al_3Mg_2$	$e_1\varepsilon_8E_1\varepsilon_1e_1$
19. Liq. $\rightleftharpoons Mg_2Si + Al_3Mg_2$	$e_2\varepsilon_8E_1\varepsilon_2e_2$
II. Lines of Tertiary Crystallization	
1. Liq. $\rightleftharpoons Al + Si + CuAl_2$	ε_4E_3
2. Liq. $\rightleftharpoons Al + Si + W$	E_3P_3
3. Liq. $\rightleftharpoons Al + CuAl_2 + W$	E_3P_2
4. Liq. $\rightleftharpoons Si + CuAl_2 + W$	$E_3\varepsilon_7$
5. Liq. $\rightleftharpoons Al + Si + Mg_2Si$	ε_5P_3
6. Liq. $+ Mg_2Si \rightleftharpoons Al + W$	$P_3\pi_5P_2$ with maximum temperatures at the point π_3
7. Liq. $+ Mg_2Si \rightleftharpoons Si + W$	$P_3\pi_5$
8. Liq. $\rightleftharpoons Al + CuAl_2 + Mg_2Si$	$P_2\varepsilon_9E_2$ with maximum temperature at the point ε_9
9. Liq. $+ Mg_2Si \rightleftharpoons CuAl_2 + W$	$P_2\pi_4$
10. Liq. $\rightleftharpoons Al + CuAl_2 + S$	ε_3E_2
11. Liq. $\rightleftharpoons Al + Mg_2Si + S$	$E_2\varepsilon_{10}P_1$ with maximum temperature at the point ε_{10}
12. Liq. $\rightleftharpoons CuAl_2 + Mg_2Si + S$	$E_2\varepsilon_8$
13. Liq. $\rightleftharpoons Al + Mg_2Si + T$	P_2E_1
14. Liq. $+ S \rightleftharpoons Al + T$	π_1P_1
15. Liq. $+ S \rightleftharpoons Mg_2Si + T$	$P_1\pi_2$
16. Liq. $\rightleftharpoons Al + T + Al_3Mg_2$	ε_1E_1
17. Liq. $\rightleftharpoons Al + Mg_2Si + Al_3Mg_2$ ...	ε_2E_1
18. Liq. $\rightleftharpoons T + Mg_2Si + Al_3Mg_2$	$E_1\varepsilon_8$

At the bottom of Fig. 3 the arrows ($\downarrow$) indicate the direction of the phase compositions and nonvariant points that lie beyond the protion of the concentration tetrahedron shown in the figure.

The region of primary crystallization of Phase U begins at about 54% Al and below in the Al - Cu - Mg sustem. In this same system, the region of concentrations that include equilibrium with the Al_3Mg_4 compound lies along its Al – Mg binary edge below 62.4% Al (a composition that corresponds to the compound Al_3Mg_2). Investigation of equilibria in the quaternary system of which these phases (U and Al_3Mg_4) form a part was not part of our job.

The corresponding concentration regions have been enclosed by wavy lines

in Fig. 3 and in the 60% and 50% Al cross-section diagrams (Figs. 7 and 8) to denote the fact that they have not been explored.

The locations of the cross sections I – I, II – II,..., IX – IX and the lines of intersection of the planes with the surfaces of secondary crystallization and the faces of the secondary tetrahedra have been drawn on the planes corresponding to 90, 80, 70, 60, and 50% Al (Fig. 3).

a) Description of the Diagrams of Plane Cross Sections

90% Al Plane

The whole cross-sectional plane lies in the region of primary crystallization of Al. The regions of secondary crystallization are bounded by the lines $_5P_3$, P_3E_3, $_4E_3$, E_3P_2, E_3P_3, P_3P_2, P_2E_2, $E_2{}_3$, E_2P_1, P_1, P_1E_1, $_1E_1$, $_2E_1$ of tertiary crystallization in the cross section. The isotherms SiP_3, SiE_3, $CuAl_2E_3$, $CuAl_2P_2$, $CuAl_2E_2$, Mg_2SiP_3, Mg_2SiP_2, Mg_2SiE_2, Mg_2SiP_1, Mg_2SiE_1, WE_3, WP_2, WP_3, SE_2, SP_1; TE_1; $Al_3Mg_2E_1$ of tertiary crystallization, corresponding to the temperatures of the nonvariant points, bound the cross-sectional plane in the region of tertiary crystallization. The straight lines SiW, $CuAl_2W$, Mg_2SiW, $Mg_2SiCuAl_2$, Mg_2SiS, Mg_2SiT are the intersections of the cross section with the faces of the secondary tetrahedra.

In accordance with what has already been said and with the following description of the cross section, the diagram of the cross section comprises the following crystallization surfaces, which are the boundaries of the coresponding crystallization spaces (Table 3).

The regions of peritectic transformations of Mg_2Si and S are the most intricate part of the cross-section diagram.

According to Table 3, the transformation from Mg_2Si to W in the concentration region within the cross section may occur by way of the following reactions:

$$\text{Liq.} + Mg_2Si \rightleftharpoons Al + W$$

$$\text{Liq.} + Mg_2Si \rightleftharpoons Al + Si + W,$$

$$\text{Liq.} + Mg_2Si \rightleftharpoons Al + CuAl_2 + W.$$

We trace the surfaces of the beginning and end of these transformations on the cross-section diagram, (Fig. 4).

The Liq. + $Mg_2Si \rightleftharpoons$ Al + W Transformation

This four-phase reaction begins at the $Mg_2SiP_3P_2Mg_2Si$ surface after completion of the Liq. $\rightleftharpoons$ Al + Mg_2Si secondary crystallization. It concludes in the WP_3P_2W concentration region with the transformation of all the Mg_2Si crystals that had separated out during secondary crystallization. The equilibrium is now a three-phase one: Liq. $\rightleftharpoons$ Al + W. The surface WP_3P_2W of the end of the four-phase reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + W is thus likewise the surface of the beginning of secondary crystallization: Liq. $\rightleftharpoons$ Al + W. In this sense, it therefore has the same value as the $P_3E_3P_2P_3$ surface, with the sole difference that on the latter the secondary crystallization: Liq. $\rightleftharpoons$ Al + W begins directly after the primary crystallization Liq. $\rightleftharpoons$ Al.

In the $Mg_2SiP_2WMg_2Si$ region the crystals of Mg_2Si remaining after the Liq + $Mg_2Si \rightleftharpoons$ Al + W transformation continue to undergo transformation in

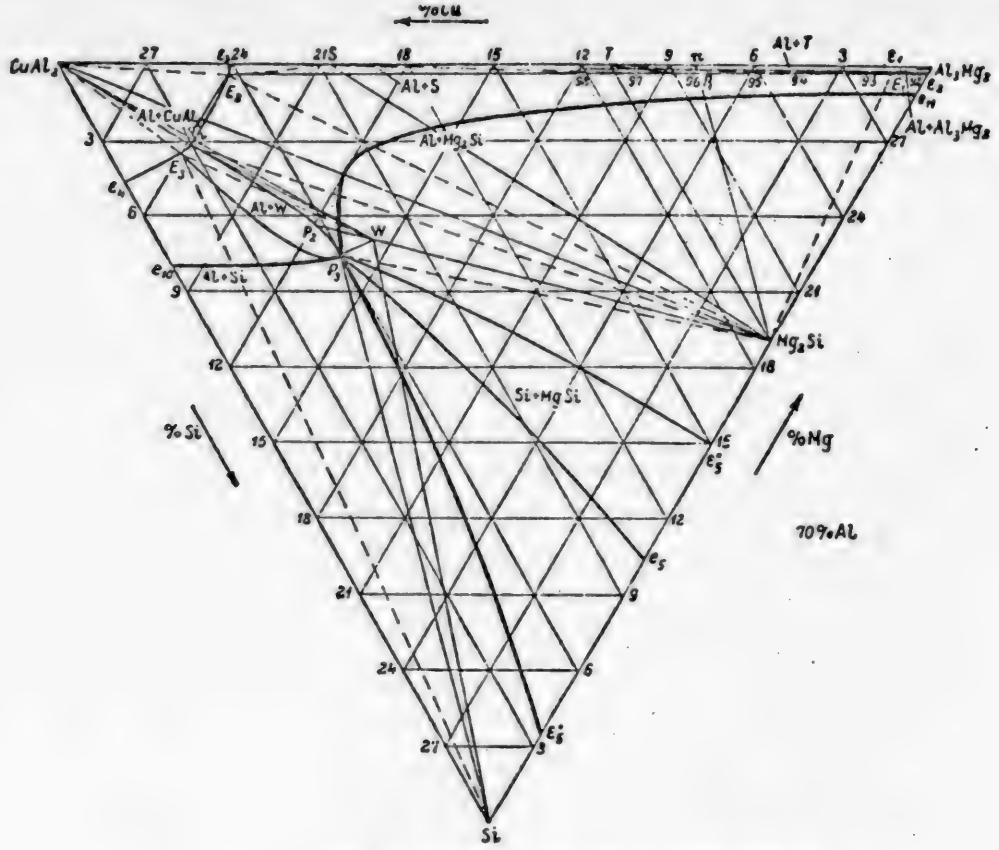

Fig. 6 Diagram of the 70% Al Cross Section

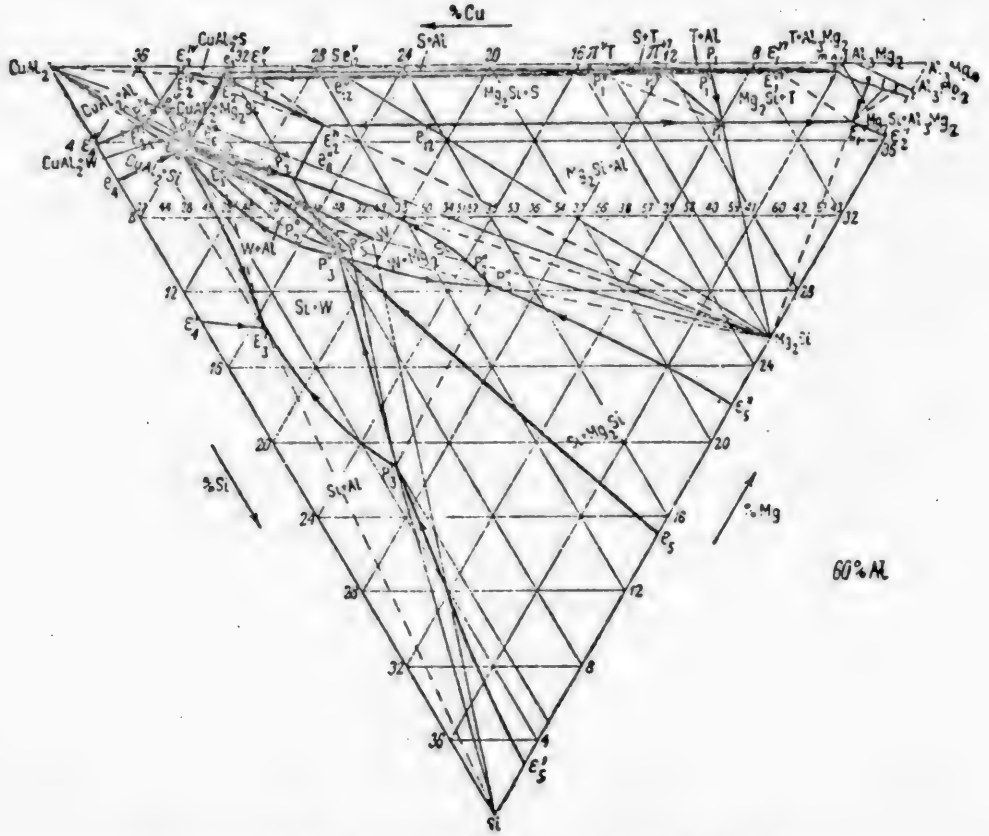

Fig. 7 Diagram of the 60% Al Cross Section

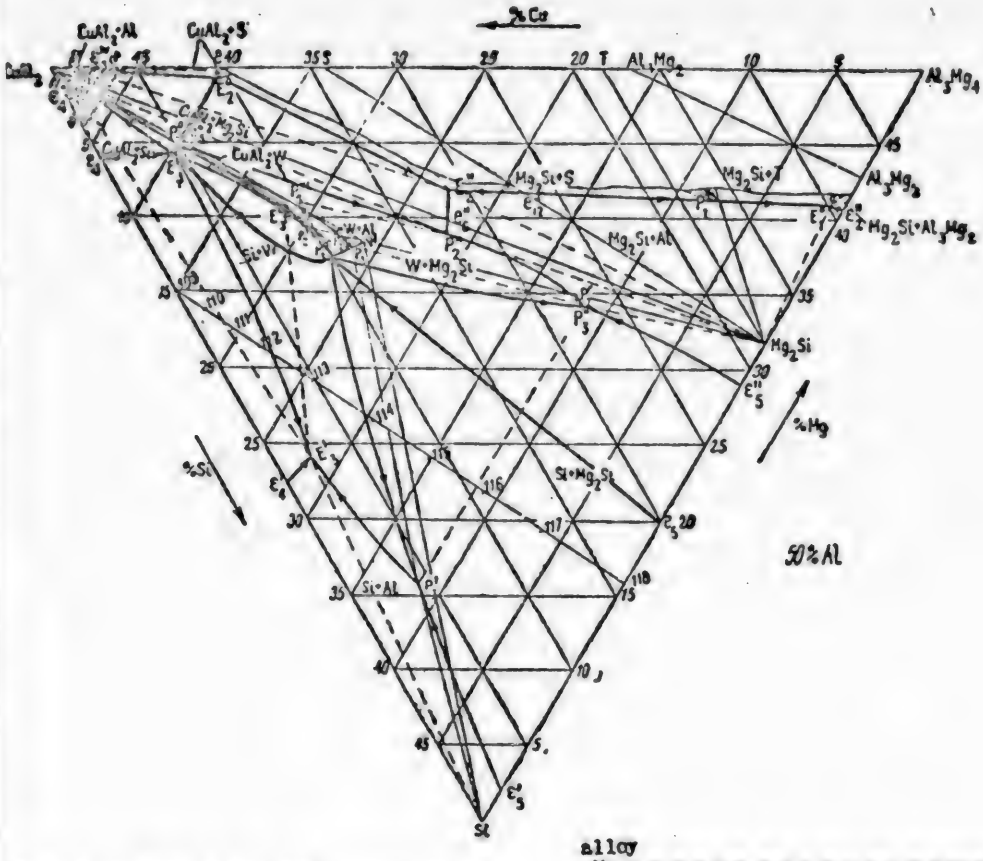

Fig. 8 Diagram of the 50% Al Cross Section

Жидкость
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} = liquid

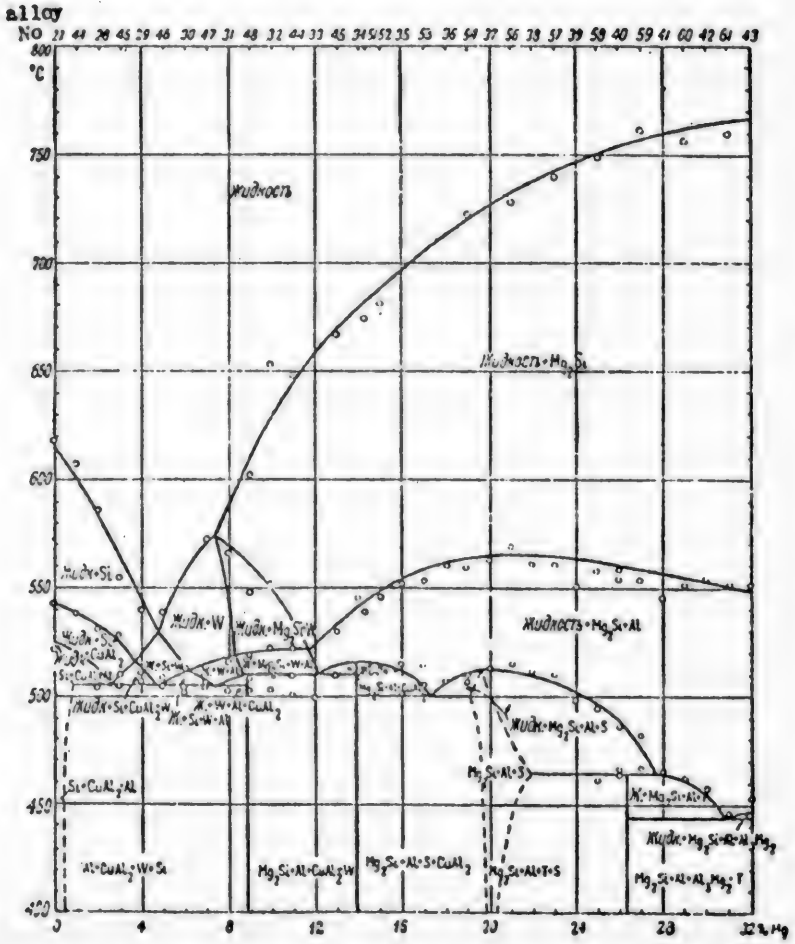
alloy No
°C
Жидкость
Жидкость • Mg_2Si
Жидкость • $Mg_2Si \cdot Al$
Жидк • W
Жидк • Mg_2Si
Жидк • $Mg_2Si \cdot S$
Жидк • $Mg_2Si \cdot Al \cdot S$
Жидк • $Mg_2Si \cdot Al \cdot Al_3Mg_2$
$Si \cdot CuAl_2 \cdot Al$
$Al \cdot CuAl_2 \cdot W \cdot Si$
$Mg_2Si \cdot Al \cdot CuAl_2 \cdot W$
$Mg_2Si \cdot Al \cdot S \cdot CuAl_2$
$Mg_2Si \cdot Al \cdot T \cdot S$
$Mg_2Si \cdot Al \cdot Al_3Mg_2 \cdot T$
%Mg

Fig. 9 Diagram of Cross Section I (60% Al, 8% Si).

TABLE 3

Crystallization Surfaces in the Diagram of the 90% Al Cross-Section Plane

Equilibria	Crystallization Surfaces
I. Primary Crystallization	
1. Liq. $\rightleftharpoons$ Al	$CuAl_2Al_3Mg_2Si$
II. Secondary Crystallization	
1. Liq. $\rightleftharpoons$ Al + Si	$Si\varepsilon_5P_3E_3\varepsilon_4Si$
2. Liq. $\rightleftharpoons$ Al + $CuAl_2$	$CuAl_2\varepsilon_4E_3P_2E_2\varepsilon_3CuAl_2$
3. Liq. $\rightleftharpoons$ Al + W	$WP_3E_3P_2W$
4. Liq. $\rightleftharpoons$ Al + Mg_2Si	$\varepsilon_5P_3P_2E_2P_1E_1\varepsilon_2\varepsilon_5$
5. Liq. $\rightleftharpoons$ Al + S	$\varepsilon_3E_2P_1\pi\varepsilon_3$
6. Liq. $\rightleftharpoons$ Al + T	$TP_1E_1\varepsilon_1T$
7. Liq. $\rightleftharpoons$ Al + Al_3Mg_2	$Al_3Mg_2\varepsilon_1E_1\varepsilon_2Al_3Mg_2$
III. Tertiary Crystallization	
1. Liq. $\rightleftharpoons$ Al + Si + Mg_2Si.....	$Mg_2SiP_3SiMg_2Si$
2. Liq. $\rightleftharpoons$ Al + Si + W	SiE_3WSi
3. Liq. $\rightleftharpoons$ Al + Si + $CuAl_2$	SiE_3CuAl_2Si
4. Liq. $\rightleftharpoons$ Al + $CuAl_2$ + W	$CuAl_2E_3WCuAl_2$
5. Liq. $\rightleftharpoons$ Al + $CuAl_2$ + Mg_2Si	$CuAl_2P_2Mg_2SiE_2CuAl_2$ with maximum temperature at the line $CuAl_2Mg_2Si$
6. Liq. + Mg_2Si $\rightleftharpoons$ Al + W	$Mg_2SiP_3P_2Mg_2Si$ – beginning of peritectic transformation (with maximum temperature at the line $MgSi\pi_5$)
	WP_3P_2W – end of peritectic transformation (with maximum temperature at the line $W\pi_5$)
7. Liq. $\rightleftharpoons$ Al + $CuAl_2$ + S	$CuAl_2E_2SCuAl_2$
8. Liq. $\rightleftharpoons$ Al + Mg_2Si + S	$Mg_2SiE_2SP_1Mg_2Si$ with maximum temperature at the line SMg_2Si
9. Liq. + S $\rightleftharpoons$ Al + T	$SP_1\pi S$ – beginning of peritectic trans.
. . . . .	$TP_1\pi T$ – end of peritectic transformation
10. Liq. $\rightleftharpoons$ Al + Mg_2Si + T	$Mg_2SiE_1TMg_2Si$
11. Liq. $\rightleftharpoons$ Al + T + Al_3Mg_2	$TE_1Al_3Mg_2T$
12. Liq. $\rightleftharpoons$ Al + Mg_2Si + Al_3Mg_2..	$Mg_2SiE_1Al_3Mg_2Mg_2Si$
IV. Quaternary Crystallization	
1. Liq. $\rightleftharpoons$ Al + Si + $CuAl_2$ + W ..	$SiWCuAl_2$
2. Liq. + Mg_2Si $\rightleftharpoons$ Al + Si + W ..	SiP_3WMg_2SiSi – beginning of peritectic transformation
	SiP_3WSi – end of peritectic transformation

Table 3 continued

Equilibria	Crystallization Surfaces
3. Liq. + $Mg_2Si \rightleftharpoons Al + CuAl_2 + W$ ..	$CuAl_2P_2WMg_2SiCuAl_2$ – beginning of peritectic transformation
	$CuAl_2P_2WCuAl_2$ – end of peritectic trans.
4. Liq. $\rightleftharpoons Al + CuAl_2 + Mg_2Si + Si$.	$CuAl_2Mg_2SiSCuAl_2$
5. Liq. + S $\rightleftharpoons Al + Mg_2Si + T$	SMg_2SiP_1TS – beginning of peritectic transformation
	$Mg_2SiP_1TMg_2Si$ – end of peritectic transformation
6. Liq. $\longrightarrow Al + T + Al_3Mg_2 + Mg_2Si$	$Mg_2SiTAl_3Mg_2Mg_2Si$

accordance with the five-phase reaction: Liq. + $Mg_2Si \rightleftharpoons Al + CuAl_2 + W$; in the $Mg_2SiP_3WMg_2Si$ region they undergo transformation in accordance with the nonvariant reaction: Liq. + $Mg_2Si \rightleftharpoons Al + Si + W$.

The Liq. + $Mg_2Si \rightleftharpoons Al + Si + W$ Transformation

This nonvariant reaction takes place at constant temperature on the $Mg_2SiWP_3SiMg_2Si$ peritectic plane. In the WP_3SiW region of this plane it terminates in the complete disappearance of the Mg_2Si crystals. Solidification continues in accordance with the four-phase reaction: Liq. $\rightleftharpoons Al + Si + W$. Thus, the WP_3SiW portion of the peritectic plane $Mg_2SiWP_3SiMg_2Si$ is likewise the surface where the tertiary crystallization: Liq. $\rightleftharpoons Al + Si + W$ begins. In this respect it has the same value as the SiE_3P_3Si plane, with the sole difference that on the latter the tertiary crystallization Liq. $\rightleftharpoons Al + Si + W$ begins directly after the secondary crystallization: Liq. $\rightleftharpoons Al + Si$.

All the liquid disappears, and solidification is concluded on the Mg_2SiWSi portion of the peritectic plane, owing to the peritectic transformation.

The Liq. + $Mg_2Si \rightleftharpoons Al + CuAl_2 + W$ Transformation

This transformation takes place on the $Mg_2SiCuAl_2P_2WMg_2Si$ peritectic plane. In the $CuAl_2P_2WCuAl_2$ portion of this plane, the reaction transforms all the Mg_2Si crystals, and solidification then continues in accordance with the four-phase reaction: Liq. $\rightleftharpoons Al + CuAl_2 + W$. Hence, the $CuAl_2P_2WCuAl_2$ portion of the peritectic plane is likewise the plane at which the tertiary crystallization: Liq. $\rightleftharpoons Al + CuAl_2 + W$ begins, and in this respect it has the same value as the $CuAl_2E_3P_2CuAl_2$ plane, on which the tertiary crystallization Liq. $\rightleftharpoons Al + CuAl_2 + W$ begins immediately after the Liq. $\rightleftharpoons Al + CuAl_2$ secondary crystallization.

Owing to nonvariant transformation, all the liquid disappears on the $Mg_2SiCuAl_2WMg_2Si$ portion of the peritectic plane, and solidification is concluded there. The same sequence of equilibria that was observed in the transition from Mg_2Si to W also takes place in the S and T transformations.

The 80% Al Plane

The plane of this cross section differs from the preceding one in that it passes through the regions of primary crystallization of three phases: Al, Si, and Mg_2Si.

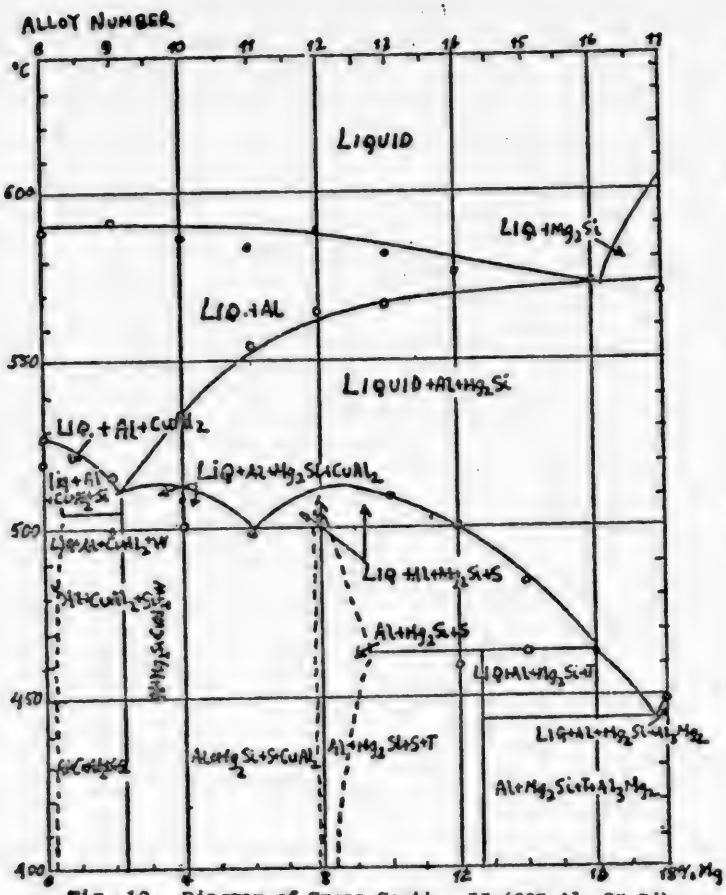

Fig. 10. Diagram of Cross Section II (80% Al, 2% Si)

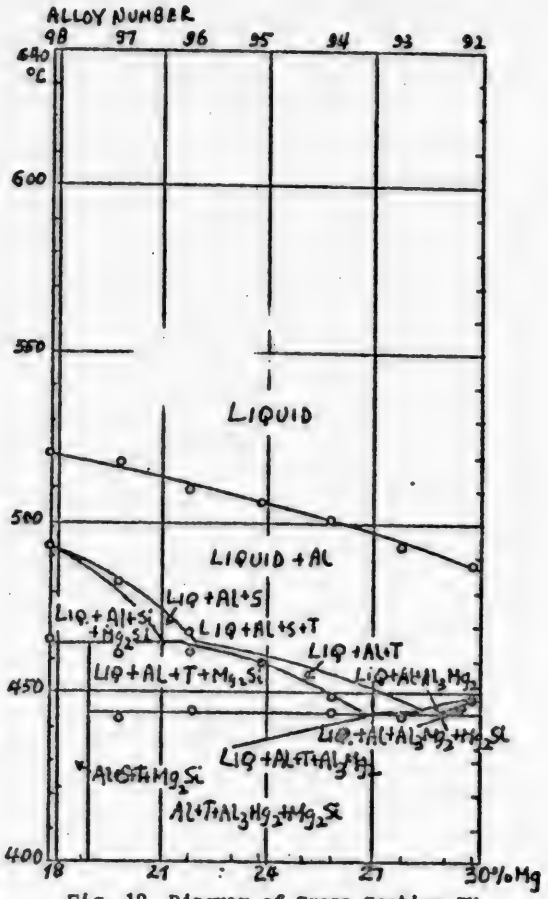

Fig. 12 Diagram of Cross Section IV (70% Al, 0.2% Si)

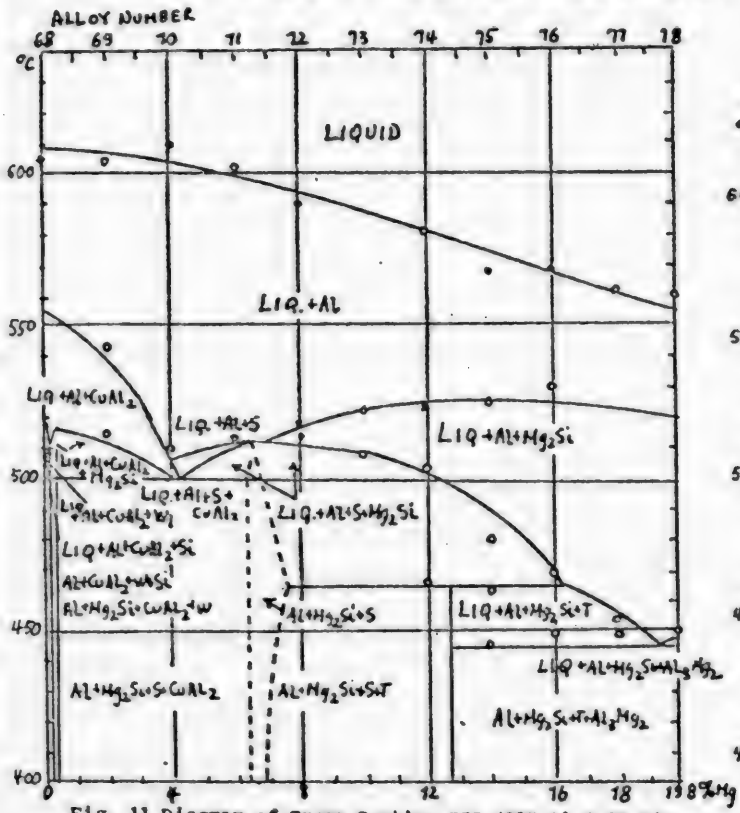

Fig. 11 Diagram of Cross Section III (80% Al, 0.2% Si)

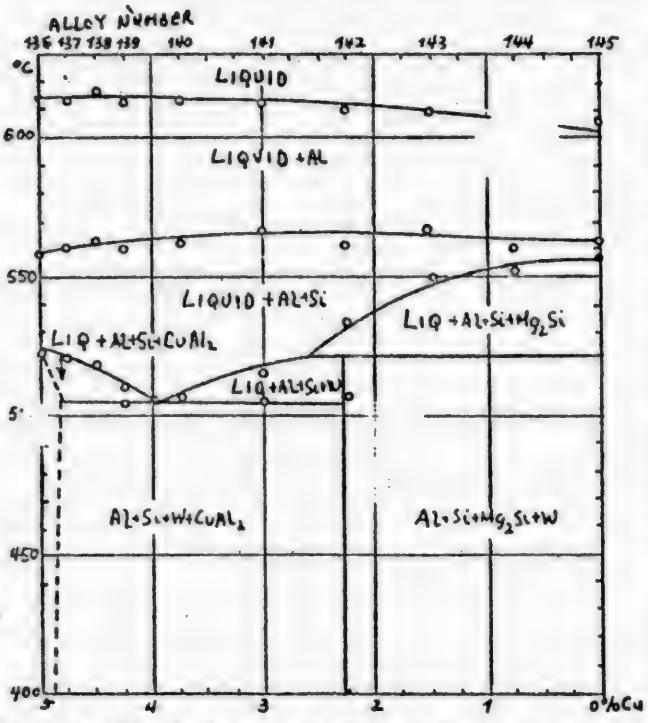

Fig. 13 Diagram of Cross Section V (90% Al, from 5% Cu and 5% Si to 0% Cu and 8% Si)

Accordingly, five new lines $e_{10}\varepsilon_5^o$, $e_{11}\varepsilon_5^o$, $e_5\varepsilon_5^o$, $\varepsilon_5'\varepsilon_5^o$, and $\varepsilon_5''\varepsilon_5^o$ and three new planes appear in the cross section diagram, their meaning being described in Table 4.

Otherwise, this cross section resembles the preceding cross section for 90% Al.

TABLE 4

Auxiliary Crystallization Surfaces on the 80% Al Cross Section

Equilibria	Crystallization Surfaces
I. Primary Crystallization	
Liq. $\rightleftharpoons$ Si	$Sie_{10}\varepsilon_5^o e_5 Si$
Liq. $\rightleftharpoons$ Mg_2Si	$e_5\varepsilon_5^o\ e_{11}e_5$
II. Secondary Crystallization	
Liq. $\rightleftharpoons$ Si + Mg_2Si	$\varepsilon_5'\varepsilon_5^o\varepsilon_5''\varepsilon_5'$

The 70% Al Plane

The cross section at 70% Al resembles that at 80% Al, differing from it only in the distribution of the regions of primary crystallization of Si and Mg_2Si, which now occupy a large part of the cross section.

The peritectic point P_3 lies on this cross-section plane (cf Table 1 for the location of the nonvariant points).

The 60% Al Plane

The cross section at 60% Al is a eutectic section with respect to Al. It passes through the regions of primary crystallization of Mg_2Si, $SiCuAl_2$, W, S, T, and Al_3Mg_2 and presents a much more intricate equilibrium picture than the preceding cross sections.

The cross-section diagram comprises the following crystallization surfaces (Table 5).

TABLE 5

Crystallization Surfaces in the Diagram of the 60% Al Cross-Section Plane

Equilibria	Crystallization surfaces
I. Primary Crystallization	
1. Liq. $\rightleftharpoons$ Si	$Sie_5P_3^oE_3^oe_4Si$
2. Liq. $\rightleftharpoons$ $CuAl_2$	$CuAl_2e_4E_3^oP_2^oE_2^oe_3CuAl_2$
3. Liq. $\rightleftharpoons$ W	$P_3^oP_3''P_2''P_2^oE_3^oP_3^o$
4. Liq. $\rightleftharpoons$ Mg_2Si	$e_5P_3^oP_2^oE_2^oP_1^opte_5$
5. Liq. $\rightleftharpoons$ S	$e_3E_2^oP_1^op_1e_3$
6. Liq. $\rightleftharpoons$ T	π^{VI}, P^{VI}, P°, $pm \approx \pi^{VI}$

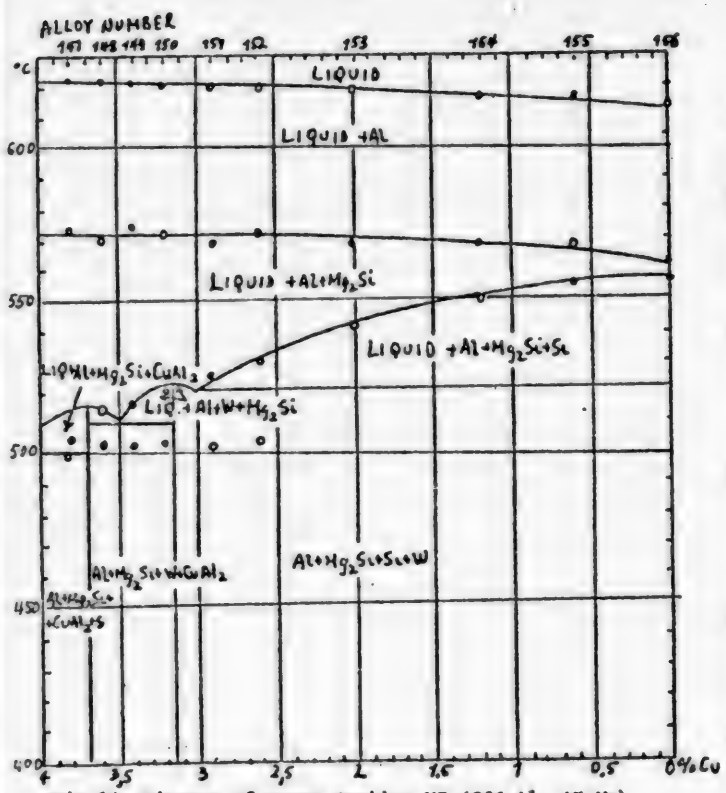

Fig 14 Diagram of Cross Section VI (90% Al, 4% Mg)

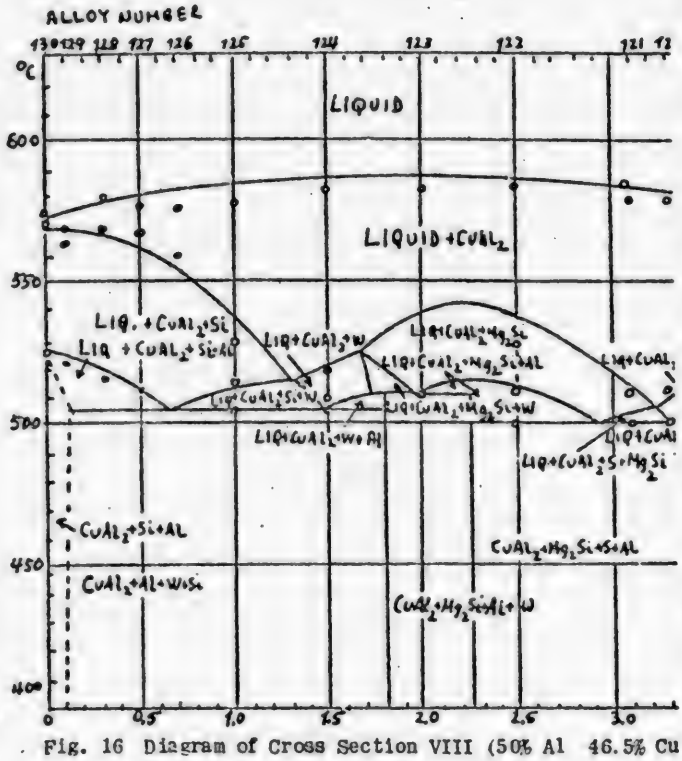

Fig. 16 Diagram of Cross Section VIII (50% Al 46.5% Cu

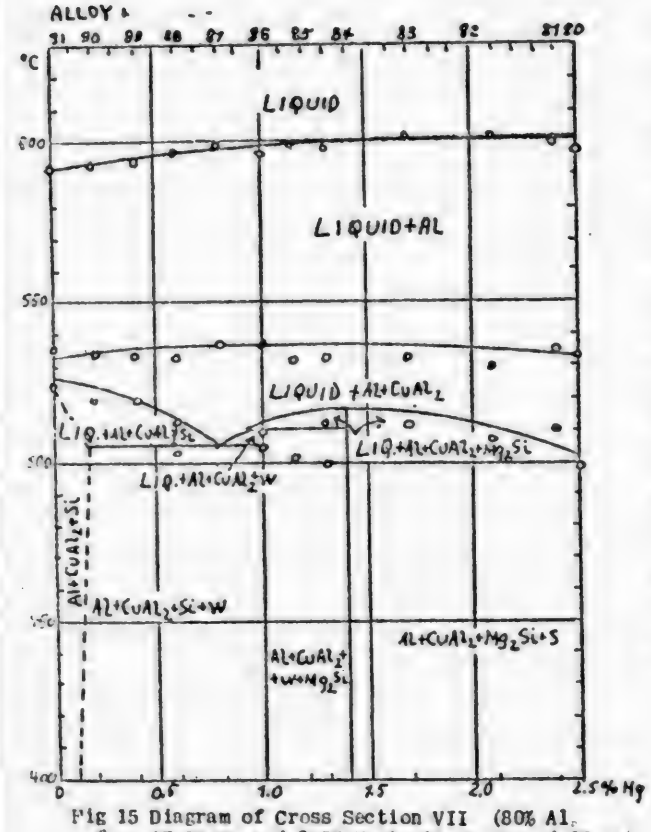

Fig 15 Diagram of Cross Section VII (80% Al, from 17.3% Cu and 2.5% Mg to 18.5% Cu and 0% Mg)

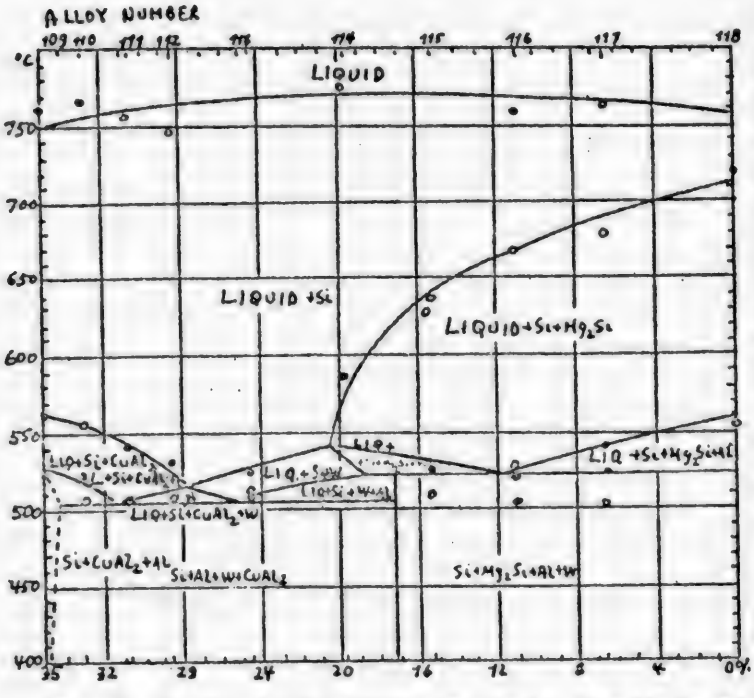

Fig. 17 Diagram of Cross Section IX (50% Al. from 35% Cu and 15% Si to 16% Mg and 34% Si)

Table 5 (continued)

Equilibria	Crystallization surfaces
II. Secondary Crystallization	
1. Liq. $\rightleftharpoons$ Si + Al	$Si\varepsilon_5^{\prime}P_3^{\prime}E_3^{\prime}\varepsilon_4^{\prime}Si$
2. Liq. $\rightleftharpoons$ $CuAl_2$ + Al	$CuAl_2\varepsilon_4^{IV}E_3^{IV}P_2^{IV}E_2^{IV}\varepsilon_5{}^{IV}CuAl_2$
3. Liq. $\rightleftharpoons$ W + Al	$P_3^{\prime}WP_2^{\prime\prime}E_2^{\prime\prime}P_3^{\prime\prime}$
4. Liq. $\rightleftharpoons$ $CuAl_2$ + Si	$\varepsilon_4^{IV}E_3^{IV}E_3^{\circ}E_3^{\prime}\varepsilon_4^{\prime}\varepsilon_4^{IV}$
5. Liq. $\rightleftharpoons$ $CuAl_2$ + W	$P_2^{IV}E_3^{IV}E_3^{\circ}E_3^{\prime\prime\prime}P_2^{\prime\prime\prime}P_2^{IV}$
6. Liq. $\rightleftharpoons$ Si + W	$P_3^{\prime}E_3^{\prime}E_3^{\circ}E_3^{\prime\prime\prime}P_3^{\prime\prime\prime}P_3^{\prime}$
7. Liq. $\rightleftharpoons$ Mg_2Si + Al	$\varepsilon_5^{\prime}P_3^{\prime}P_2^{\prime}E_2^{\prime}P_1^{\prime}E_1^{\prime}\varepsilon_2^{\prime}\varepsilon_5^{\prime}$
8. Liq. $\rightleftharpoons$ Si + Mg_2Si	$\varepsilon_5^{\prime}P_3^{\prime}P_3^{\circ}P_3^{\prime\prime}\varepsilon_5^{\prime\prime}\varepsilon_5^{\prime}$
9. Liq. + Mg_2Si $\rightleftharpoons$ W	$P_2^{\prime\prime}p_2^{\prime\prime}P_3^{\prime\prime}P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2^{\prime\prime}$ – beginning of peritectic transformation (with maximum temperature at the line $p_2^{\prime\prime}p_2^{\circ}$)
	$P_2^{\prime\prime\prime}p_2^{\prime\prime\prime}P_3^{\prime\prime\prime}P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2^{\prime\prime}$ – end of peritectic transformation (with maximum temperature at the line $p_2^{\prime\prime\prime}P_2^{\circ}$
10. Liq. $\rightleftharpoons$ $CuAl_2$ + $MgSi_2$.....	$E_2^{IV}P_2^{IV}{}^{\circ}P_2^{\prime\prime}P_2^{\prime\prime}E^{\prime\prime}E_2^{\circ}E_2^{IV}$ with maximum temperature at the line $e_8^{IV}e_8^{\circ}e_8^{\prime\prime}$
11. Liq. $\rightleftharpoons$ S + Al	$\varepsilon_3^{V}E_2^{V}P_1^{V}\pi^{V}\varepsilon_3^{V}$
12. Liq. $\rightleftharpoons$ $CuAl_2$ + S	$\varepsilon_3^{IV}E_2^{IV}E_2^{\circ}E_2^{V}\varepsilon_3^{VI}\varepsilon_3^{IV}$
13. Liq. $\rightleftharpoons$ Mg_2Si + S	$P_1^{V}E_2^{V}E_2^{\circ}E_2^{\prime\prime}P_1^{\prime\prime}P_1^{\circ}P_1^{V}$ with maximum temperature at the line $e_{12}^{V}e_{12}^{\circ}e_{12}^{\prime\prime}$
14. Liq. $\rightleftharpoons$ T + Al	$TP_1^{VI}E_1^{VI}\varepsilon_1^{VI}T$
15. Liq. + S $\rightleftharpoons$ T	$\pi^{V}P_1^{V}P_1^{\circ}p_1\approx^{V}$ – beginning of peritectic transformation
	$\pi^{VI}P_1^{VI}P_1^{\circ}p_1\pi^{VI}$
16. Liq. $\rightleftharpoons$ Mg_2Si + T	$P_1^{VI}E_1^{VI}\alpha qE_1^{\prime\prime}P_1^{\circ}P_1^{VI}$
17. Liq. $\rightleftharpoons$ T + Al_3Mg_2	$\varepsilon_1^{IV}E_1^{VI}o\ m\varepsilon_1^{VI}$
18. Liq. $\rightleftharpoons$ Mg_2Si + Al_3Mg_2	$qE_1^{\prime\prime}\varepsilon_2^{\prime\prime}\ tq$
III. Tertiary Crystallization	
1. Liq. $\rightleftharpoons$ Si + Al + $CuAl_2$.....	$SiE_3^{\prime}E_3^{VI}CuAl_2Si$
2. Liq. $\rightleftharpoons$ $CuAl_2$ + Al + W	$CuAl_2E_3^{IV}E_3^{\prime\prime\prime}WCuAl_2$
3. Liq. $\rightleftharpoons$ Si + Al + W	$SiE_3^{\prime}E_3^{\prime\prime\prime}WSi$
4. Liq. $\rightleftharpoons$ $CuAl_2$ + W + Si	$E_3^{IV}E_3^{\prime\prime\prime}E_3^{\prime}E_3^{IV}$
5. Liq. $\rightleftharpoons$ Si + Mg_2Si + Al	$SiP_3^{\prime}P_3^{\prime\prime}Mg_2SiSi$
6. Liq. + Mg_2Si $\rightleftharpoons$ Al + W	$Mg_2SiP_3^{\prime\prime}P_3^{\prime\prime\prime}p_2^{\prime\prime\prime}P_2^{\prime\prime\prime}P_2^{\prime\prime}Mg_2Si$ – beginning of peritectic transformation (with maximum temperature at the line $Mg_2Sip_2^{\prime\prime\prime}$)

Table 5 (continued)

Equilibria	Crystallization surfaces
	$WP_3'''p_2''\pi'P_2'''W$ – end of peritectic transformation (with maximum temperature at the line Wp_2'''
7. Liq. + $Mg_2Si \rightleftharpoons Si + W$	$P_3'P_3'''P_3^{\circ}P_3'P_3''$ – beginning of peritectic transformation
	$P_3'''P_3^{\circ}P_3'$ – end of peritectic transformation
8. Liq. $\rightleftharpoons CuAl_2 + Mg_2Si + Al$ ...	$CuAl_2P_2^{IV}{}''P_2Mg_2SiE_2^2E_2^{IV}CuAl_2$ with maximum temperature at the line $CuAl_2Mg_2Si$
9. Liq. + $Mg_2Si \rightleftharpoons CuAl_2 + W$	$P_2'P_2^{IV}P_2^{\circ}P_2'''P_2''$ – beginning of peritectic transformation
	$P_2'''P_2^{\circ}P_2^{IV}P_2'''$ – end of peritectic transformation
10. Liq. $\rightleftharpoons CuAl_2 + S + Al$	$CuAl_2E_2^{IV}E_2^{V}SCuAl_2$
11. Liq. $\rightleftharpoons Mg_2Si + S + Al$.....	$Mg_2SiE_2''E_2^{V}SP_1^{V}P_1''Mg_2Si$ with maximum temperature at the line Mg_2SiSi
12. Liq. $\rightleftharpoons CuAl_2 + Mg_2Si + S$	$E_2^{IV}E_2''\,E_2^{V}E_2^{IV}$
13. Liq. $\rightleftharpoons Mg_2Si + T + Al$	$Mg_2SiE_1''E_1^{VI}TMg_2Si$
14. Liq. + S $\rightleftharpoons$ Al + T	$SP_1^{V}P_1^{VI}\pi^{VI}S$ – beginning of peritectic transformation
	$TP^{VI}\pi^{VI}T$ – end of peritectic transformation
15. Liq. + S $\rightleftharpoons Mg_2Si + T$.....	$P_1^{V}P_1''P_1^{\circ}P_1^{VI}P_1^{V}$ – beginning of peritectic transformation
	$P_1''P_1^{VI}P_1^{\circ}P_1''$ – end of peritectic transformation
16. Liq. $\rightleftharpoons Mg_2Si + Al_3Mg_2 + Al$ ..	$sE_1''Mg_2Sits$
17. Liq. $\rightleftharpoons T + A\text{-}_3Mg_2 + Al$	$TE_1^{VI}{}_{nm}T$
18. Liq. $\rightleftharpoons Mg_2Si + T + Al_3Mg_2$....	$E_1''E_1^{VI}{}_{ns}E_1''$
IV. Quaternary Crystallization	
1. Liq. $\rightleftharpoons$ Si + Al + $CuAl_2$ + W ...	$SiCuAl_2WSi$
2. Liq. + $Mg_2Si \rightleftharpoons$ Si + Al + W ...	$Mg_2SiWP_3'''P_3'SiMg_2Si$ – beginning of peritectic transformation
	$WP_3\ P_3\ SiW$ – end of peritectic transformation
3. Liq. + $Mg_2Si \rightleftharpoons CuAl_2$ + Al + W	$Mg_2SiWP_2'''P_2^{IV}CuAl_2Mg_2Si$ – beginning of peritectic transformation
	$WP_2\ P_2\ CuAl_2W$ – end of peritectic transformation
4. Liq. $\rightleftharpoons CuAl_2 + Mg_2Si$ + S + Al	$CuAl_2Mg_2Si\ S\ CuAl_2$

Table 5 (Continued)

Equilibria	Crystallization Surfaces
5. Liq. + S $\rightleftharpoons$ Mg_2Si + Al + T	$SMg_2SiP_1''P_1^{VI}TS$ – beginning of peritectic transformation $TP_1^{VI}P_1''Mg_2SiT$ – end of peritectic transformation
6. Liq. $\rightleftharpoons$ Mg_2Si + T + Al + Al_3Mg_2	$TMg_2SiAl_3Mg_2A_2T$

The regions of the peritectic transformations of Mg_2Si and S constitute the most complex portion of the cross-section diagram.

According to Table 5, the transformation of Mg_2Si into W in the concentration region within the cross section can be effected by way of the following reactions:

1) Liq. + Mg_2Si $\rightleftharpoons$ W,
2) Liq. + Mg_2Si $\rightleftharpoons$ Al + W,
3) Liq. + Mg_2Si $\rightleftharpoons$ Si + W,
4) Liq. + Mg_2Si $\rightleftharpoons$ $CuAl_2$ + W,
5) Liq. + Mg_2Si $\rightleftharpoons$ Si + Al + W,
6) Liq. + Mg_2Si $\rightleftharpoons$ $CuAl_2$ + Al + W.

We outline the surfaces of the beginning and end of these transformations on the cross-section diagram.

The Liq. + Mg_2Si $\rightleftharpoons$ W Transformation

This three-phase reaction commences on the $P_2''p_2''P_3''P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2''$ plane after the primary crystallization of Mg_2Si.

In the $P_2'''p_2'''P_3'''P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2'''$ concentration region this three-phase reaction ends at the $P_2'''p_2'''P_3'''P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2'''$ with the transformation of all the primary crystals of Mg_2Si that have settled out. This does not conclude the formation of W crystals; they continue to be formed, but now solely from the liquid phase. The $P_2^{IV}p_2^{IV}P_3^{IV}P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2^{IV}$ surface of the end of the three-phase reaction: Liq. + Mg_2Si $\rightleftharpoons$ W is thus also the surface of the beginning of the primary crystallization of W and in this respect has the same significance as the $P_3^{\circ}P_2^{\circ}E_3^{\circ}P_3^{\circ}$ plane. The only difference between them is that on the latter the primary crystallization of W commences directly from the liquid, whereas the primary crystallization of W on the $P_2^{V}p_2^{V}P_3^{V}P_3^{\circ}p_2^{\circ}P_2^{\circ}P_2^{V}$ plane is preceded by the primary crystallization of Mg_2Si and the transformation of this phase into W.

The primary crystals of Mg_2Si left after the transformation in accordance with the reaction: Liq. + Mg_2Si $\rightleftharpoons$ W, continue to undergo transformation in the $p_3^{V}p_3^{V}p^{\circ}p^{\circ}$ region in accordance with the four-phase reaction: Liq. + + Mg_2Si $\rightleftharpoons$ Si + W; in the $P''P_3'''p_2'''P_2'''P_2''P_2''P_3''$ region in accordance with the reaction: Liq. + Mg_2Si $\rightleftharpoons$ Al + W, and in the $P_2''P_2^{\circ}P_2''$ region in accordance with the Liq. + Mg_2Si $\rightleftharpoons$ $CuAl_2$ + W reaction.

The Liq. + Mg_2Si $\rightleftharpoons$ Al + W Transformation

The transformation commences at the $Mg_2SiP_3^{V}P_3''p_2''P_2''P_2^{V}Mg_2Si$ surface after the second eutectic crystallization: Liq. $\rightleftharpoons$ Mg_2Si + Al in the $Mg_2SiP_3^{V}p''P_2^{V}Mg_2Si$ concentration region and after the secondary eutectic crystallization of Liq. + Mg_2Si $\rightleftharpoons$ W in the $P_3^{V}p_2^{V}P_2^{V}P_2''p_2''P_3''P_3^{V}$ concentration region. It ends in the $WP_3''p_2''P_2''W$ concentration region with the transformation of all the crystals of Mg_2Si that had separated out earlier. We now have a

three-phase equilibrium: Liq. $\rightleftharpoons$ Al + W. The $WP_3P_2'''P_2W$ surface of the end of the four-phase reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + W is thus likewise the surface of the beginning of the secondary crystallization Liq. $\rightleftharpoons$ Al + W. Hence, it has the same significance as the surface $P_3'''P_2'''E_3P_3'''$, with the sole difference that on the latter the secondary crystallization begins immediately after the primary crystallization of W. The crystals of Mg_2Si left after transformation in accordance with the reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + W continue to undergo transformation in accordance with the non-variant five-phase reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + Si + W in the $Mg_2SiP_3''P_3'''WMg_2Si$ region, and in accordance with the nonvariant reaction: Liq. + $Mg_2Si \rightleftharpoons Al + CuAl_2 + W$ in the $Mg_2SiP''P_2'''WMg_2Si$ region.

The Liq. + $Mg_2Si \rightleftharpoons$ S + W Transformation

This transformation, beginning at the $P_3''P_3'''P_3^{\circ}P_3'P_3''$ surface, concludes with the complete disappearance of the Mg_2Si that had previously separated out on the $P_3'''P_3^{\circ}P_3'$ surface, and the four-phase equilibrium gives way to a three-phase one: Liq. $\rightleftharpoons$ Si + W. Thus, the $P_3'''P_3^{\circ}P_3'$ surface is also a surface where three-phase equilibrium begins. In the $P_3'P_3''p_3'p_3''$ region the transformation of Mg_2Si is not completed, continuing in accordance with the nonvariant reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + Si + W.

The Liq. + $Mg_2Si \rightleftharpoons CuAl_2$ + W Transformation

Beginning at the $P_2''P_2^{IV}P_2^{\circ}P_2'''P_2''$ surface, this transformation ends at the $P_2''P_2^{\circ}P_2^{IV}P_2''$ surface with the total disappearance of the Mg_2Si crystals, being replaced by the three-phase equilibrium: Liq. $\rightleftharpoons CuAl_2$ + W, at the same surface. In the concentration region $P_2^{IV}P_2''P_2''P_2^{IV}$, the transformation of the Mg_2Si does not come to an end, but continues in accordance with the nonvariant reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + $CuAl_2$ + W.

The Liq. + $Mg_2Si \rightleftharpoons$ Si + Al + W Transformation

This nonvariant transformation takes place at constant temperature on the peritectic plane $Mg_2SiWP_3''P_3'SiMg_2Si$. In the $WP_3'''P_3SiW$ portion of this plane it ends with the complete disappearance of the crystals of Mg_2Si, giving way to a four-phase reaction: Liq. $\rightleftharpoons$ Si + Al + W. Owing to nonvariant transformation, all the liquid disappears in the $Mg_2SiWSiMg_2Si$ portion of the peritectic plane, and solidification comes to an end in this area.

The Liq. + $Mg_2Si \rightleftharpoons CuAl_2$ + Al + W Transformation

This nonvariant transformation takes place on the peritectic plane $Mg_2SiWP_2''P_2^{IV}CuAl_2Mg_2Si$. In the $WP_2'''P_2^{IV}CuAl_2W$ portion of the plane it ends with the complete disappearance of the crystals of Mg_2Si, being replaced by the four-phase reaction: Liq. $\rightleftharpoons CuAl_2$ + Al + W. Nonvariant transformation causes all the liquid to disappear in the $Mg_2SiWCuAl_2Mg_2Si$ portion of the plane, and solidification comes to an end.

The 50% Al Plane

The diagram of this cross section differs in no essential particular from that of the preceding cross section. As the cross section passes through the concentration tetrahedron at lower Al percentages, the regions of secondary and tertiary crystallization are noticeably contracted in this phase.

b) Description of the Linear Sections of the Al – Cu – Mg – Si Tetrahedron, Investigated to Plot the Structural Diagram

All the sections described below were investigated by thermal and microscopic methods of analysis. Only Cross Section I on the 60% Al plane is illustrated with microphotographs here.

The other cross sections were not microphotographed.

The first four cross sections I, II, III, and IV were investigated principally to determine the position of the monovariant curves directly adjoining the Al-Cu-Mg face of the tetrahedron. The other five cross sections – V to IX – were selected so as to facilitate plotting the other monovariant curves in the tetrahedron.

I. Cross Section I: 8% Si on the 60% Al Plane.

a) Cross-Section Diagram

The location of the cross section on the plane is shown in Fig. 7 together with composition of the alloys investigated.

The cross section diagram, shown in Fig. 9, was plotted from the cooling curves and the results of microscopic examination.

The cross section crosses three regions of primary crystallization: Mg_2Si, W, and Si. Correspondingly, the liquidus line is represented on the cross section by three intersecting curves.

The region of primary crystallization of Mg_2Si is bounded on the bottom by two lines of secondary crystallization:

1) the eutectic line, at which the dual eutectic Mg_2Si + Al begins to separate out after the primary crystallization of the Mg_2Si is complete; and

2) the transition (peritectic) line, at which the transformation of the initially formed crystals of Mg_2Si begins in accordance with the reaction: Liq. + $Mg_2Si \rightleftharpoons$ W.

The region of the primary crystallization of W is bounded by three lines of secondary crystallization:

1) at the right by the transition line, at which there ends the transformation of Mg_2Si according to the reaction: Liq. + $Mg_2Si \rightleftharpoons$ W after the primary crystallization of the Mg_2Si, a transformation that began at the curve above (which lies the region: Liq. + Mg_2Si + W; and 2) at the bottom by two eutectic lines, at which, after the primary crystallization of W, there begins the separation of the binary eutectics W + Al and W + Si.

The region of primary crystallization of Si is bounded at the bottom by two eutectic lines of secondary crystallization, at which the binary eutectics Si + W and Si + $CuAl_2$ begin to separate out after the primary crystallization of Si is complete.

The region of the secondary eutectic crystallization of Mg_2Si + Al is bounded at the bottom by five lines of tertiary crystallization: 1) four eutectic lines, at which the secondary crystallization of Mg_2Si + Al is followed by the separation of the ternary eutectics: a) Mg_2Si + Al + Al_3Mg_2; b) Mg_2Si + + Al + T; c) Mg_2Si + Al + S along the line with the maximum-temperature point corresponding to the intersection of the cross section with maximum-temperature line SMg_2Si in Fig. 7; and d) Mg_2Si + Al + $CuAl_2$ in Fig. 7; and 2) the transition line at which, after the secondary crystallization of Mg_2Si + Al, there

begins the transformation of Mg_2Si according to the reaction: Liq. + $Mg_2Si \rightleftharpoons$ $\rightleftharpoons$ Al + W.

The region of secondary peritectic crystallization Liq. + $Mg_2Si \rightleftharpoons W$ is bounded at the bottom by a line of tertiary peritectic crystallization at which there begins the transformation of Mg_2Si in accordance with the four-phase reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + W, which previously took place in accordance with the reaction Liq. + $Mg_2Si \rightleftharpoons W$.

The region of secondary eutectic crystallization Liq. $\rightleftharpoons$ W + Al is bounded by three lines of tertiary crystallization: 1) at the right by a transition line, at which the transformation of Mg_2Si according to the peritectic reaction Liq. + $Mg_2Si \rightleftharpoons$ Al + W, which began at the curve that is the upper boundary of the temperature region of this reaction, is concluded; and 2) at the bottom by two eutectic lines, at which the ternary eutectics: W + Al + $CuAl_2$ and W + Si + Al begin to separate out after the secondary crystallization Liq. $\rightleftharpoons$ W + Al is complete.

The region of the secondary eutectic crystallization Liq. $\rightleftharpoons$ Si + W is bounded at the bottom by two eutectic lines of tertiary crystallization, at which the ternary eutectics Si + W + Al and Si + W + $CuAl_2$ separate out after completion of the secondary crystallization Liq. $\rightleftharpoons$ Si + W.

The region of the secondary eutectic crystallization Liq. $\rightleftharpoons$ Si + $CuAl_2$ is bounded at the bottom by two eutectic lines of tertiary crystallization, at which the ternary eutectics Si + $CuAl_2$ + W and Si + $CuAl_2$ + Al begin to separate out after the secondary crystallization Liq. $\rightleftharpoons$ Si + $CuAl_2$.

On this cross section the solidus line is represented by the lines denoting the end of crystallization of the ternary eutectics Si + $CuAl_2$ + Al and Mg_2Si + Al + S and by five horizontal straight lines corresponding to three nonvariant eutectic crystallization reactions of the quaternary eutectics: a) Al + $CuAl_2$ + W + Si; b) Mg_2Si + Al + S + $CuAl_2$, c) Mg_2Si + Al + Al_3Mg_2 + T; and two peritectic transformations: a) Liq. + $Mg_2Si \rightleftharpoons$ Al + $CuAl_2$ + W and b) Liq. + S $\rightleftharpoons$ Mg_2Si + Al + T.

b) Microphotography of the Cross Section

The alloy with 32% Mg at the extreme right of the cross section is a ternary alloy belonging to the Al-Mg-Si system. According to Hanson and Gayler's structural diagram [8], it is in the region of the primary deposition of Mg_2Si. This primary crystallization within the alloy is followed by the separation of the binary eutectic Mg_2Si + Al and, lastly, the ternary eutectic Mg_2Si + Al + Al_3Mg_2.

Fig. 18 shows the macrostructure of this alloy; it clearly discloses the liquation of the Mg_2Si by specific gravity. Lighter than the rest of the mother-liquid phase, the Mg_2Si separates out in the form of primary crystals that float and all congregate in the upper half of the ingot. As a result, the microstructure of the alloy varies, depending upon whether it represents the upper (Fig. 19) or the lower (Fig. 20) part of the ingot.

The primary crystals of Mg_2Si are easily seen in the microphotograph of the upper portion of the alloy (Fig. 19); they are mostly surrounded by dendrites of aluminum. The rest of the microsection is filled with the Al_3Mg_2 phase, which is next to separate out. One gets the impression that there is no Mg_2Si + Al binary eutectic in the alloy.

The background against which the crystals are shown is customary for the microstructure of binary hypoeutectoid alloys of Al-Mg. For the sake of

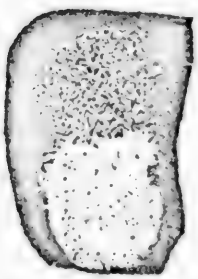

Fig. 18. 60% Al, 32% Mg, 8% Si, unetched × 1.

Fig. 19. 60% Al, 32% Mg, 8% Si; etched with 0.5% HF. × 10.

Fig. 20. 60% Al, 32% Mg, 8% Si etched with 0.5% HF. × 100.

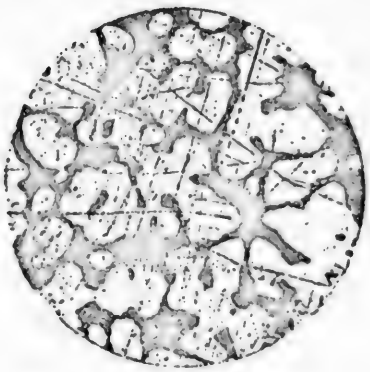

Fig. 21. 80% Al, 20% Mg; etched with 0.5% HF. × 100.

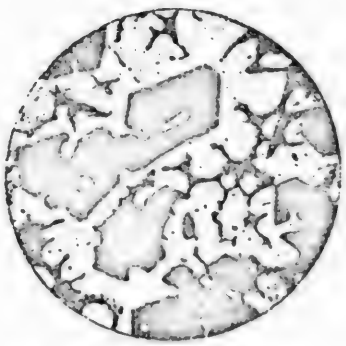

Fig. 24. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 100.

Fig. 25. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 100.

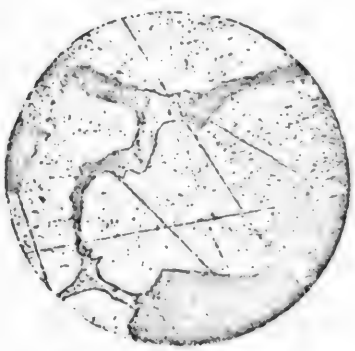

Fig. 28. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 330.

Fig. 26. 80% Al, 17% Mg, 3% Si; etched with 0.5% HF. × 100.

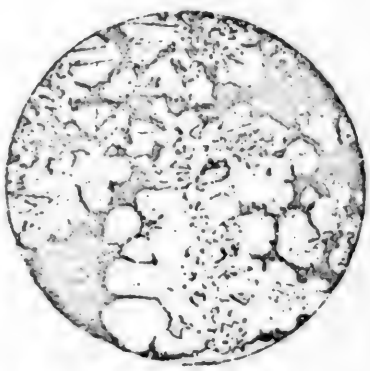

Fig. 27. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 100.

comparison, a microphotograph of an alloy of this sort with 20% Mg is shown in Fig. 21. Owing to the fact that the composition of the binary eutectic Al + Al_3Mg_2 (35% Mg) is very close to that of the compound Al_3Mg_2 (37.6% Mg), which therefore constitutes the predominant portion of the eutectic (moreover, Al_3Mg_2 has a lower specific gravity and hence occupies a relatively large area on the polished section), the phases constituting the eutectic crystallize separately. The aluminum, which separates out at the eutectic temperature, crystallizes at the faces of its primary dendrites, prolonging them, whereas the Al_3Mg_2 solidifies thereafter, occupying the remaining free space.

There are no primary crystals of Mg_2Si (cf Fig. 29) in the microphotograph of the bottom part of the ingot (Fig. 20). But the "crystals" of the binary eutectic Mg_2Si + Al, which are not present at all in the upper part of the ingot (Fig. 19), are clearly visible. The boundary at which the "crystals" of the binary eutectic Mg_2Si + Al vanish as we proceed from the bottom of the ingot toward its top, being replaced by the growing crystals of Mg_2Si, is very clearly marked. This is beautifully shown, for example, in the microphotographs of quaternary alloys with 30% Mg (Fig. 29) and 22% Mg (Fig. 35) along Cross Section I.

In the upper half of the ingot the Mg_2Si that crystallizes secondarily is doubtless deposited at the faces of the crystals that were deposited primarily, so that there is not binary eutectic structure. The Mg_2Si that is deposited tertiarily also crystallizes at the faces of the primary crystals in the upper portion of the ingot, but in the bottom part of the ingot it crystallizes at the faces of the crystals that settled out during the crystallization of the binary eutectic. This evidently is the reason why the individual faces of the Mg_2Si dendrites are not surrounded by Al but are in contact with the Al_3Mg_2.

The liquation of the Mg_2Si by density does not affect the temperature or the course of the subsequent reactions that occur in the alloy as cooling continues, unless its crystals are transformed in a peritectic reaction (or form solid solutions).

As a matter of fact, say, in the crystallization of the mixture m (Fig. 22), the deposited crystals B are liquated, since they are of different density from the rest of the liquid phase. No matter whether all the crystals congregate at the bottom or the top part of the solidifying ingot or are uniformly distributed throughout its volume, the liquid phase will attain the composition of the point l at the temperature that corresponds to that point, and a binary eutectic will begin to crystallize throughout its volume. The structure of the alloy will merely differ in various parts of the ingot, as was the case with the Al-Mg-Si alloys.

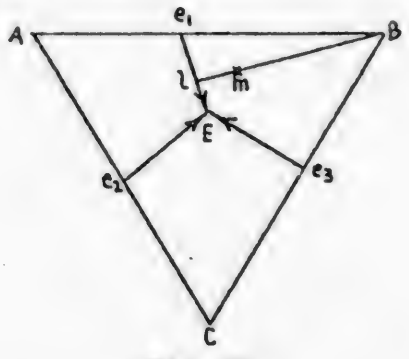

Fig. 22.

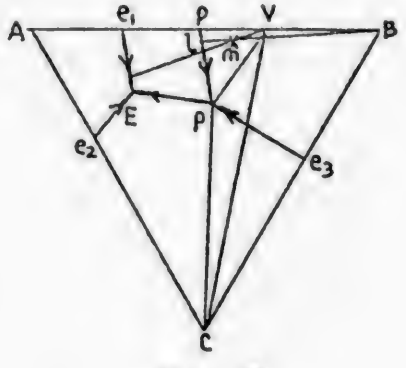

Fig. 23.

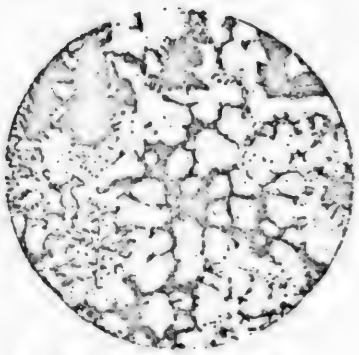

Fig. 29. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 100.

Fig. 30. 60% Al, 30% Mg, 8% Si; etched with 0.5% HF. × 330.

Fig. 31. 60% Al, 28% Mg, 8% Si; etched with 0.5% HF. × 100.

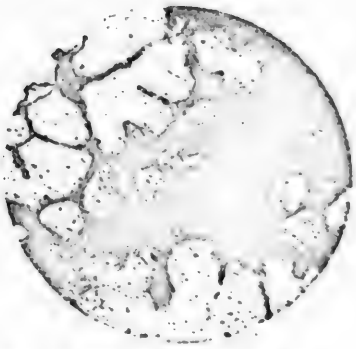

Fig. 32. 60% Al, 26% Mg, 8% Si; etched with 0.5% HF. × 157.

Fig. 33. 60% Al, 22% Mg, 8% Si; etched with 0.5% HF. × 100.

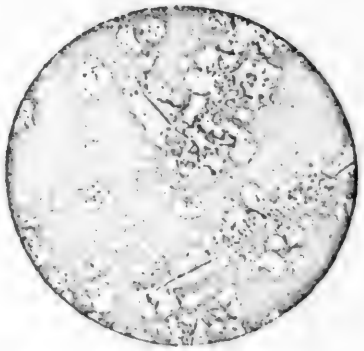

Fig. 34. 60% Al, 22% Mg, 8% Si; etched with 0.5% HF. × 100.

Fig. 35. 60% Al, 22% Mg, 8% Si, etched with 0.5% HF. × 100.

Fig. 36. 60% Al, 22% Mg, 8% Si; etched with 0.5% HF. × 100.

Fig. 37. 60% Al, 22% Mg, 8% Si; etched with 0.5% HF. × 100.

Matters are otherwise, if the liquating phase (B) is transformed during the subsequent cooling, as, for example, in the case shown in Fig. 23. When the liquid reaches the point 1, it takes on the composition of the point 1 everywhere, at the temperature corresponding to the point 1, as was the case in the instance just considered. But the reaction B + Liq. $\rightleftharpoons$ W, which should take place after the primary crystallization B, will take place only in that region of the bath where the B crystals that first separated out are present.

Let us assume that after primary crystallization is complete, all the concentrations from the point B to 1 are encountered along the section of the solidifying ingot, owing to the density liquation that takes place. In such a case it may be stated that the location of the point m will differ for different ingot sections. In the very top portion of the ingot, where the deposited B crystals are concentrated, it will lie near the point B, i.e., it will lie within the triangle VBC; in the lower layers it may lie within the triangle VPC or, lastly, within the region VPp. Finally, in the very bottom layers, where there are no B crystals at all, the point m will coincide with the point 1.

When that is so, it may happen that four different structures will be encountered in the ingot if cooling is rapid enough, depending upon whether: 1) at the very top, the transformation of B ends with the four-phase reaction B + Liq. $\rightleftharpoons$ V + C, with the liquid disappearing (i.e., the structure will correspond to that of the alloys within VBC); 2) in layers that are somewhat lower, the transformation of B will end with a four-phase reaction and the disappearance of B, but solidification will continue, with the binary eutectic V + C separating out along the curve PE, after which the ternary eutectic V + C + A will separate out (i.e., the structure will correspond to that of the alloys within VPC). Still lower down, the transformation of B will end in a three-phase reaction: B + Liq. $\rightleftharpoons$ V, and solidification continues; or 3) with the separation of the binary eutectic along the curve PE, followed by that of the ternary eutectic V + C + A; or 4) the separation of the binary eutectic V + A along the curve e_1E, followed by that of the ternary eutectic V + C + A.

In our case, such complex relationships during cooling, due to the liquidation of the Mg_2Si, can occur only in the concentration range from ~14 to ~7.4% Mg. In all alloys within the concentration range of 32 to 14% Mg, where the Mg_2Si is not transformed, its liquation cannot affect the succeeding equilibria.

Now let us turn to further study of the alloy microstructure.

The microstructures of an alloy with 30% mg are shown in Figs. 24-25 and 27-30. According to the cross-section diagram, this alloy ought to solidify with the deposition of: 1) primary Mg_2Si crystals; 2) a binary eutectic Mg_2Si + + Al; 3) a ternary eutectic Mg_2Si + Al + T; and 4) a quaternary eutectic Mg_2Si + + Al + T + Al_3Mg_2.

The microphotographs of this alloy, taken in the upper part of the ingot (Figs. 24 and 25) clearly show the Mg_2Si crystals formed, surrounded with aluminum crystallized in a binary eutectic with Mg_2Si.

The ternary eutectic Mg_2Si + Al + T solidified in between the crystals of aluminum. In this structural component, only two phases Al and T are actually visible, and it wholly resembles the binary eutectic Al + T that crystallizes in the Al-Cu-Mg ternary system when no Si is present.

For the sake of comparison, a microphotograph of the ternary alloy Al·Cu·Mg with 17% Mg and 3% cu is given in Fig. 26. According to the structural diagram of Al-Cu-Mg (Fig. 1), the Al + T binary eutectic (the dark constituent

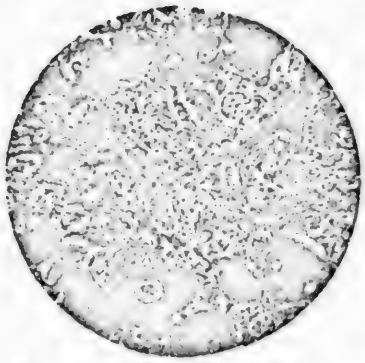

Fig. 38. 60% Al, 19% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

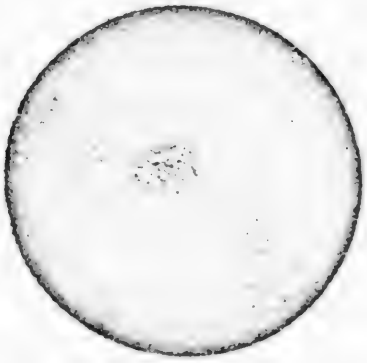

Fig. 39. 60% Al, 19% Mg, 8% Si; etched with 10% NaOH 80° C. × 1200.

Fig. 40. 60% Al, 4% Mg, 36% Cu; etched with 10% NaOH 80° C. × 2000.

Fig. 41. 60% Al, 17% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

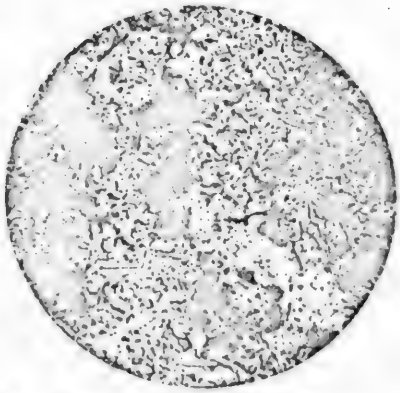

Fig. 42. 60% Al, 17% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

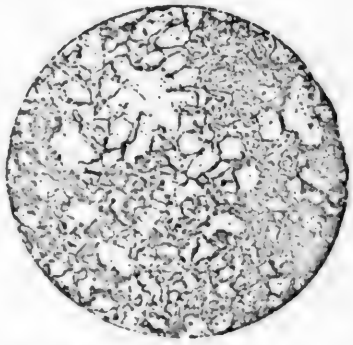

Fig. 43. 60% Al, 14% Mg, 8% Si; etched with 0.5% HF. × 100.

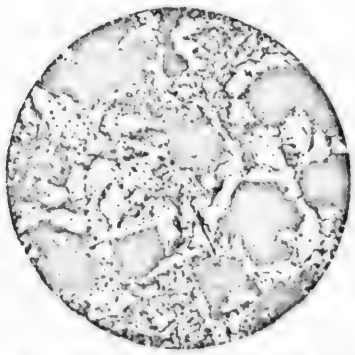

Fig. 44. 60% Al, 11.5% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

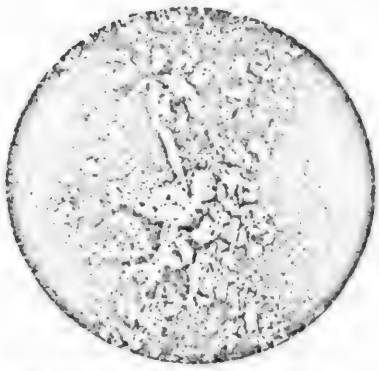

Fig. 45. 60% Al, 11.5% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

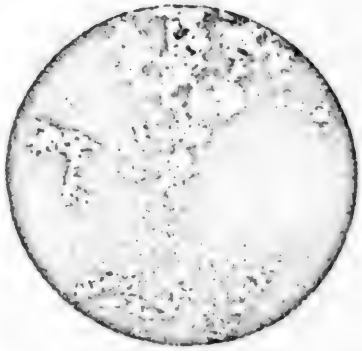

Fig. 46. 60% Al, 11.5% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

in between the primary crystals – when etched with 0.5%HF, T is colored light brown, the thin light veins on the dark background being aluminum) crystallizes at this concentration after the primary deposition of Al. In the same section particles of Al_3Mg_2 (light) are also seen in between the primary crystals; they crystallize after the deposition of the binary eutectic, as is seen from the freely formed faces of the latter's "crystals". The Al_3Mg_2 particles are one of the components and the predominant constituent of the Al + T + Al_3Mg_2 ternary eutectic. There is very little T and Al in this ternary eutectic. Both of these phases crystallize on crystals (T and Al) that had separated out previously, which are in contact with the Al_3Mg_2, as is clearly seen in the microphotograph. The crystallization sequence of the three phases in the eutectic is doubtless Al, T, and Al_3Mg_2.

As has already been stated, the ternary eutectic Mg_2Si + Al + T in the quaternary alloy (Fig. 25) actually consists of two phases: Al and T. The Mg_2Si in the ternary eutectic doubtless crystallizes on its grains that settled out earlier, which are usually in contact on their larger or smaller surface with the "rivers" of Al + T.

In this alloy, too, the Al_3Mg_2 phase constitutes a quaternary eutectic, crystallizing last in a nonvariant reaction as in the ternary alloy (Fig. 26), and solidifying in the remaining available spaces. This phase is visible in Figs. 24 and 25 as bright particles in between the crystals of aluminum, contrasting with the dark T. The Al_3Mg_2 crystals are best seen in Fig. 27, which is a microphotograph of the bottom of the alloy. At the left of this figure it is seen that the Al_3Mg_2 is in simultaneous contact with the Mg_2Si, Al, and T (cf also Fig. 30). This is also seen in the microphotograph of the upper portion of the ingot (Fig. 25).

The overall picture is clearer in the high magnification of Fig. 28, taken at the top of the ingot.

Fig. 29 is a microphotograph of an alloy with 30% Mg at the boundary of the liquation zone. Primary crystals of Mg_2Si are visible at the top, but absent at the bottom; there we see, however, the well-formed "crystals" of the binary eutectic Al + Mg_2Si.

The microstructure of an alloy with 28% Mg (Fig. 31) is in no way different from that of an alloy with 30% Mg, which has just been discussed in detail.

In an alloy with 26% Mg (Fig. 32) a ternary eutectic Mg_2Si + Al + S crystallizes after the primary crystallization of Mg_2Si and the separation of the binary eutectic Mg_2Si + Al. In this ternary eutectic, as in the preceding one, Mg_2Si is not clearly visible, continuing to grow along the surfaces of previously deposited crystals during the crystallization of the ternary eutectic. Alongside the gray grains of S in the eutectic we can see the small grains of Al (quite bright). They partly adjoin the crystals of Mg_2Si. The ternary eutectic is surrounded by Al + T, formed in the nonvariant reaction S + Liq. $\rightleftharpoons$ Mg_2Si + Al + T and in the ensuing four-phase reaction Liq. $\rightleftharpoons$ Mg_2Si + + Al + T. We also see particles of Al_3Mg_2 (at the top of the figure), their presence indicating that the alloy solidified completely during the formation of the quaternary eutectic: Liq. $\rightleftharpoons$ Mg_2Si + Al + T + Al_3Mg_2.

In the alloy with 22% Mg (Figs. 33-35) the transition from S to T does not take place. Its structure comprises: the primary crystals of Mg_2Si (in Fig. 33, showing the upper portion of the ingot); the binary eutectic Mg_2Si + Al (in Fig. 34, showing the bottom of the ingot); and the ternary eutectic Mg_2Si + Al + S, from which the Mg_2Si is deposited as before, either on the

Fig. 47. 60% Al, 12% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

Fig. 48. 60% Al, 11% Mg, 8% Si; etched with 10% NaOH 80° C. × 400.

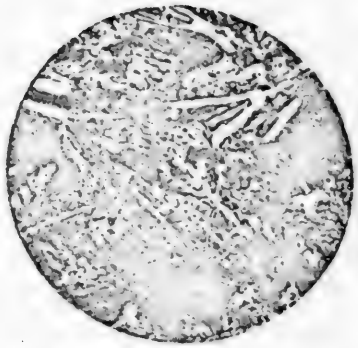

Fig. 49. 60% Al, 10% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

Fig. 50. 60% Al, 10% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

Fig. 51. 60% Al, 9% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

Fig. 52. 60% Al, 9% Mg, 8% Si; etched with 10% NaOH 80° C. × 100.

Fig. 53. 60% Al, 9% Mg, 8% Si; etched with 10% NaOH 80° C. × 1200.

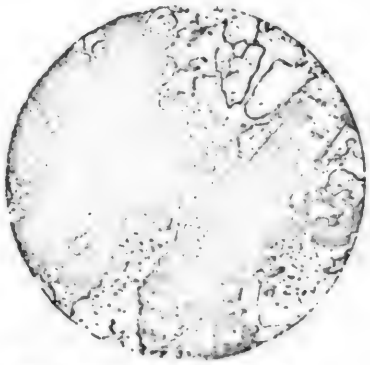

Fig. 54. 60% Al, 8% Mg, 8% Si; etched with 10% NaOH 80° C. × 400.

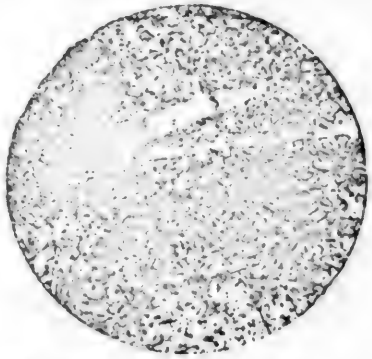

Fig. 55. 60% Al, 7% Mg, 8% Si; etched with 0.5% HF. × 100.

crystals first deposited (Fig. 33) or on the crystals formed during secondary crystallization (Fig. 34). The boundary of the Mg_2Si liquation zone is shown in Fig. 35. According to the solidification diagram (Fig. 9), the alloy solidifies completely with the formation of three phases, Mg_2Si, Al, and S, the component parts of the ternary eutectic.

The structure of an alloy with 20% Mg (Figs. 36 and 37) is in no way different from that of the preceding alloy, constituting a conglomerate of three structural constituents: 1) primary crystals of Mg_2Si; 2) the binary eutectic Mg_2Si + Al; and 3) the ternary eutectic Mg_2Si + Al + S.

In the alloy with 19% Mg (Fig. 38), there appears, in addition to these three structural constituents; a quaternary eutectic Mg_2Si + Al + $CuAl_2$. The polished section was etched with NaOH at 80°. The $CuAl_2$ in the quaternary eutectic is black (light brown under the microscope).

The dendrites of aluminum are now hard to distinguish against the general background of the polished section, since they are speckled with fine deposits of $CuAl_2$ (black), formed during the cooling of the alloy as the result of the disintegration of the solid solution. This disintegration phenomenon is also observed in alloys with higher percentages of Mg, in which S is the disintegration phase, but in the microphotographs these S particles are not visible within the aluminum dendrites, as they have almost the same color as the latter.

The structure of the quaternary eutectic Mg_2Si + Al + S + $CuAl_2$ is readily seen in the high magnification of Fig. 39. It is not at all different from that of the ternary eutectic Al + S + $CuAl_2$ in the ternary alloys Al-Cu-Mg (cf the microphotograph of a ternary alloy Al-Cu-Mg with 4% Mg in Fig. 40). In this structure three phases: Al, S, and $CuAl_2$, are closely intermixed. The Mg_2Si crystallizes out of the quaternary eutectic separately from its other constituent phases.

In an alloy with 17% Mg (Figs. 41 and 42) the structural constituents are the same as in the alloy with 19% Mg, except for the ternary eutectic, which now consists of Mg_2Si + Al + $CuAl_2$. It is readily visible in the microphotographs. The liquation of Mg_2Si is found as before. The microphotographs of Figs. 41 and 42 are the upper part of the ingot and the bottom part, respectively.

The alloy with 14% Mg is nearly on the Al-$CuAl_2$-Mg_2Si plane. It contains only three phases: Al, $Cual_2$, and Mg_2Si. In the microphotograph (Fig. 43) of the bottom portion of the ingot there are accordingly visible: the binary eutectic Mg_2Si + Al and the ternary eutectic Mg_2Si + Al + $CuAl_2$.

In the alloy with 11.5% Mg, the Mg_2Si still crystallizes first (Fig. 44) as before, but a transition reaction occurs during secondary crystallization: Mg_2Si + Liq. $\rightleftharpoons$ W. There is no more of the binary eutectic Mg_2Si + Al in the alloy (Fig. 45, bottom of the ingot).

The transition from Mg_2Si to W is clearly visible in the microphotograph of Fig. 44, as well as in the high magnification of Fig. 46.

Now the liquation of Mg_2Si results in the structure of the bottom of the ingot being completely different from that of the ingot's top. The Mg_2Si + Liq. $\rightleftharpoons$ W reaction cannot take place at all at the bottom of the liquid bath, inasmuch as all the Mg_2Si floated to the top at the beginning of this reaction. Then crystals of W will be formed as was demonstrated for the ternary system (cf Fig. 23 above), and the entire subsequent course of crystallization will be such as if the composition of the alloy corresponded to the point

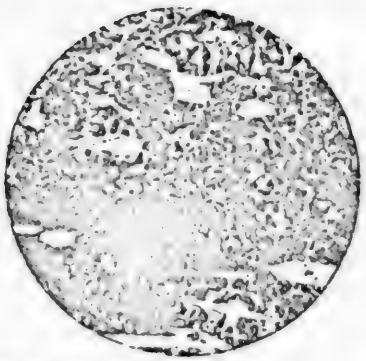

Fig . 56. 60% Al. 6% Mg. 8% Si; etched with 10% NaOH 80° C. × 100.

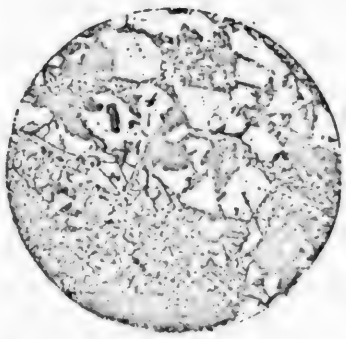

Fig. 57. 60% Al. 0% Mg. 8% Si; etched with 0.5% HF. × 100.

Fig 58. 60% Al, 0% Mg, 8% Si; etched with 0.5% HF. × 100.

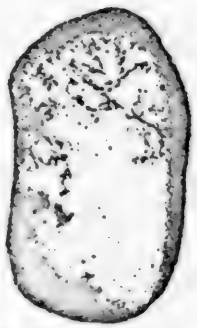

Fig 59. 60% Al. 0% Mg, 8% Si; 6ea unetched. × 1.

Fig. 60. 60% Al. 1% Mg, 8% Si; etched with 0.5% HF. × 100.

Fig 61. 60% Al. 1% Mg. 8% Si; etched with 0.5% HF. × 100.

Fig. 62. 60% Al, 2% Mg. 8% Si; etched with 0.5% HF. × 100.

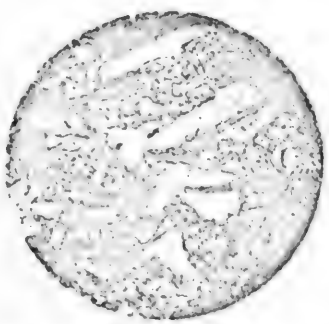

Fig. 63. 60% Al, 2% Mg. 8% Si; etched with 0.5% HF. × 100.

Fig . 64. 60% Al, 2% Mg. 8% Si; etched with 0.5% HF. × 600.

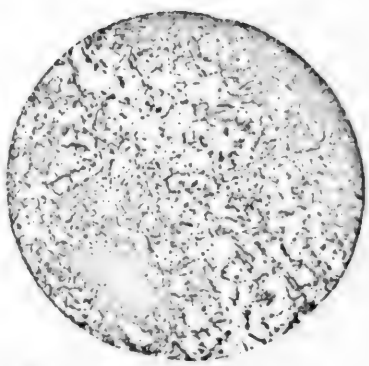

Fig 65. 60% Al. 4% Mg. 8% Si; etched with 0.5% HF. × 100.

of intersection of the Mg_2Si and W secondary crystallization curves (at about 7.4% Mg) in Fig. 9, the cross-section diagram, i.e.,

1) Liq. $\rightleftharpoons$ W,

2) Liq. $\rightleftharpoons$ W + Al,

3) Liq. $\rightleftharpoons$ W + Al + $CuAl_2$,

4) Liq. $\rightleftharpoons$ W + Al + $CuAl_2$ + Si.

Accordingly, the primary separation of W, the binary eutectic W + Al, the ternary eutectic W + Al + $CuAl_2$, and a small quantity of the quaternary eutectic W + Al + $CuAl_2$ + Si are actually visible in the bottom region (Fig. 45). In the upper portion of the ingot (Fig. 44) the W is visible principally near the Mg_2Si crystals, which it partially surrounds, but no Si is seen at all, which testifies to the absence of a quaternary eutectic. Hence, solidification ends here with a five-phase transitional reaction: Mg_2Si + Liq. $\rightleftharpoons$ W + Al + $CuAl_2$ with complete disappearance of the liquid phase.

The structure of the bottom of an alloy with 10% Mg (Fig. 50) is the same as that of an alloy with 12% Mg (Fig. 47). The veins of the quaternary eutectic with Si are more clearly visible. Fig. 49 is a microphotograph of the top part of this ingot.

The structure of an alloy with 9% Mg (Figs. 51 and 52) differs in no essential particular from that of the preceding ones, except for more W and less Mg_2Si. The structure of the quaternary eutectic is shown in Fig. 53, a microphotograph of this alloy.

In an alloy with 8% mG, Mg_2Si is the first to crystallize as before (cf. Fig. 54). There is no Si present at all where the Mg_2Si + Liq. $\rightleftharpoons$ W reaction takes place.

But at 7% Mg the first phase to crystallize is W (Fig. 55). Then W + Al crystallizes, followed by W + Si + Al and, lastly, W + Al + $CuAl_2$ + Si.

The structure of an alloy with 6% Mg does not differ from that of the previous one. Fig. 56 is a microphotograph of this alloy after etching with 10% NaOH.

The rest of the cross section can be examined conveniently, beginning with the extreme, ternary alloy Al-Cu-Si (without any Mg).

Figs. 57 and 58 are microphotographs of this alloy. In this alloy Si is the first to crystallize (Fig. 57). Si is liquated like the Mg_2Si, collecting in the upper portion of the ingot (cf. Fig. 59 for the macrostructure). But since Si does not undergo peritectic transformations, it causes no disturbance of the equilibrium during cooling. The primary crystallization of Si is followed by the crystallization of the binary eutectic Si + $CuAl_2$ and then by that of Si + $CuAl_2$ + Al.

Both structural components are readily seen in the microphotographs of the top (Fig. 57) and the bottom of the alloy (Fig. 58).

When 1% Mg is added to a ternary Al-Cu-Si alloy, no new phases make their appearance. The structure remains the same (Figs. 60 and 61). Hence, the concentration of the alloy still remains in the three-phase region Si + + $CuAl_2$ + Al as before, owing to the formation of solid solutions.

At 2% Mg (Fig. 64) a new phase appears in a quaternary eutectic. This is the quaternary phase W. The rest of this alloy's structure does not differ from that of the alloy with 1% Mg. As before, the Si, which is first to

crystallize, is liquated (see Fig. 62 for the top of the ingot and Fig. 64 for its bottom portion).

In an alloy with 4% Mg (Fig. 65) the first to crystallize is the Si, as before, followed by the binary eutectic Si + $CuAl_2$, the ternary eutectic Si + $CuAl_2$ + W, and the quaternary eutectic Si + $CuAl_2$ + W + Al.

II. Cross Section II: 2% Si on the 80% Al Plane

The location of this cross section on the plane is shown in Fig. 5, together with an indication of the compositions of the alloys investigated. The cross-section diagram is given in Fig. 10.

Most of the cross section passes through the region of the primary crystallization of Al, being hypereutectic with respect to Al only at the right, between 16 and 18% Mg.

It differs but little from the preceding section below the line of secondary eutectic crystallization of Al + Mg_2Si.

The region of the secondary eutectic crystallization of Al + $CuAl_2$ is bounded at the bottom by three lines of tertiary eutectic crystallization, at which the separation of the ternary eutectics: a) Al + $CuAl_2$ + Mg_2Si, b) Al + $CuAl_2$ + W, and c) Al + $CuAl_2$ + Si, takes place after the secondary crystallization.

The transformation of Mg_2Si into W at the cross section is confined to only one nonvariant reaction: Liq. + $Mg_2Si \rightleftharpoons$ Al + $CuAl_2$ + W on the horizontal located between $\sim$ 2 and $\sim$ 3.6% Mg.

III. Cross Section III: 0.2% Si on the 80% Al Plane

Fig. 11 is the diagram of this cross section. The location of the cross section on the plane is shown in Fig. 5.

The cross section is hypoeutectic with respect to Al. Accordingly, the curve of primary crystallization is a smooth curve on this cross section. Because of the fact that the nonvariant points E_2, P_1, and E_1 (cf Fig. 3) lie close to the Al-Cu-Mg face of the tetrahedron, this cross section, like the preceding ones, does not traverse the region of the secondary crystallization of Al with the phases Al_3Mg_2 and T, located at the Al-Cu-Mg face of the tetrahedron (cf Fig. 5), but crosses the region of the secondary crystallization of Al with phase S, located at the same face, only near the line of maximum temperature $e_{12}e_{10}$ (Fig. 3).

We omit a more detailed description of the section inasmuch as it is self-evident after the description of the two preceding cross sections.

IV. Cross Section IV: 0.2% Si on the 70% Al Plane.

The location of the cross section on the plane is shown in Fig. 6. Fig. 12 is the diagram of that part of the section which we investigated.

This section, in contrast to the two preceding ones (on the 80% Al plane), traverses the region of the secondary crystallization of Al with the phases S, T, and Al_3Mg_2, located at the Al-Cu-Mg face of the tetrahedron (cf Fig. 6).

V. Cross Section V: From 5% Cu and 5% Si to 0% Cu and 8% Si on the 90% Al Plane

The diagram of the cross section is given in Fig. 13, while its location on the plane is shown in Fig. 4.

The cross section lies within the region of the primary crystallization of Al and the region of the secondary crystallization of Al + Si. It is one of the simplest of those investigated by us. The curve of the tertiary crystallization consists of three intersecting eutectic branches, along which the separation of the ternary eutectics: Al + Si + Mg_2Si, Al + Si + W, and Al + Si + $CuAl_2$ begins after secondary crystallization is complete. Two horizontals on the cross-section diagram represent nonvariant equilibria: Liq. + + $Mg_2Si \rightleftharpoons$ Al + Si + W and Liq. $\rightleftharpoons$ Al + Si + W + $CuAl_2$.

VI. Cross Section Vi: 4% Mg on the 90% Al Plane

Fig. 14 is the diagram of the part of the cross section that we investigated; Fig. 7 shows the location of the section on the plane.

This cross section lies in the region of the primary crystallization of Al and the region of the secondary crystallization of Al + Mg_2Si.

The curve of tertiary crystallization consists of three intersecting branches: 1) the eutectic: Liq. $\rightleftharpoons$ Al + Mg_2Si + Si; 2) the peritectic: Liq. + + $Mg_2Si \rightleftharpoons$ Al + W; and 3) the eutectic Liq. $\rightleftharpoons$ Al + Mg_2Si + $CuAl_2$.

The three horizontals represent the following nonvariant equilibria: 1) Liq. + $Mg_2Si \rightleftharpoons$ Al + Si + W, 2) Liq. + $Mg_2Si \rightleftharpoons$ Al + $CuAl_2$ + W, and 3) Liq. $\rightleftharpoons$ Al + Mg_2Si + $CuAl_2$ + S.

VII. Cross Section VII: From 17.3% Cu and 2.5% Mg to 18.5% Cu and 0% Mg on the 80% Al Plane

The cross-section diagram is given in Fig. 15, and the location of the section on the plane in Fig. 5.

The whole cross section lies within the region of the primary crystallization of Al and within the region of the secondary crystallization of Al + $CuAl_2$.

The line of tertiary crystallization consists of three intersecting eutectic branches, at which the separation of the ternary eutectics: Al + $CuAl_2$ + + Mg_2SI, Al + $CuAl_2$ + W, Al + $CuAl_2$ + Si begins after the secondary crystallization of Al + $CuAl_2$ is complete. The three horizontals correspond to the nonvariant equilibria: Liq. $\rightleftharpoons$ Al + $CuAl_2$ + Mg_2Si + S; Liq. + $Mg_2Si \rightleftharpoons$ Al + $CuAl_2$ + + W; Liq. $\rightleftharpoons$ Al + $CuAl_2$ + Si + W.

VIII. Cross Section VIII: 46.5% Cu at the 50% Al Plane

Fig. 16 is the cross-section diagram; the location of the section on the plane is shown in Fig. 8.

The whole cross section passes through the region of primary crystallization of $CuAl_2$. The line of secondary crystallization consists of four intersecting eutectic branches, at which the crystallization of the binary eutectics: $CuAl_2$ + S, $CuAl_2$ + Mg_2Si, $CuAl_2$ + W, and $CuAl_2$ + Si begins after the primary crystallization of the $CuAl_2$ is complete.

The region of the secondary crystallization of $CuAl_2$ + S is bounded at the bottom by two eutectic lines of the tertiary crystallization of $CuAl_2$ + S + + Al and $CuAl_2$ + S + Mg_2Si.

The region of the secondary crystallization of $CuAl_2$ + Mg_2Si is bounded at the bottom by two eutectic lines of tertiary crystallization: $CuAl_2$ + S + + Mg_2Si and $CuAl_2$ + Mg_2Si + Al, and by the transitional line at which the Mg_2Si

that separates out during secondary crystallization is transformed into W in accordance with the reaction: Liq. + $Mg_2Si \rightleftharpoons CuAl_2 + W$.

The region of the secondary crystallization of $CuAl_2 + W$ is bounded by three lines of tertiary crystallization: at the right by a transitional line at which the transformation Liq. + $Mg_2Si \rightleftharpoons CuAl_2 + W$, which began at the curve that is the right-hand boundary of the region Liq. + $CuAl_2 + Mg_2Si + W$, is concluded, and by two eutectic lines: Liq. $\rightleftharpoons CuAl_2 + W + Al$, and Liq. $\rightleftharpoons CuAl_2 + Si + W$.

The region of the secondary crystallization: Liq. $\rightleftharpoons CuAl_2 + Si$ is bounded at the bottom by two eutectic lines of tertiary crystallization: Liq. $\rightleftharpoons CuAl_2 + Si + W$ and Liq. $\rightleftharpoons CuAl_2 + Si + Al$.

The three horizontals on the cross section correspond to the following nonvariant equilibria:

$$\text{Liq.} \rightleftharpoons CuAl_2 + Mg_2Si + S + Al,$$

$$\text{Liq.} + Mg_2Si \rightleftharpoons CuAl_2 + Al + W,$$

$$\text{Liq.} \rightleftharpoons CuAl_2 + Al + W + Si.$$

IX. Cross Section IX: From 35% Cu and 15% Si to 16% Mg and 34% Si on the 50% Al Plane

The location of the cross section on the plane is shown in Fig. 8. The cross-section diagram is given in Fig. 17.

The whole cross section lies within the region of primary crystallization of Si. The line of secondary crystallization consists of three intersecting branches: Si + Mg_2Si, Si + W, and Si + $CuAl_2$.

The region of the secondary crystallization of Si + Mg_2Si is bounded at the bottom by two lines of tertiary crystallization: the eutectic Liq. $\rightleftharpoons$ Si + Mg_2Si + Al and the transitional line Liq. + $Mg_2Si \rightleftharpoons$ Si + W.

The region of secondary crystallization of Si + W is bounded at the right by a transitional line at which the reaction: Liq. + $Mg_2Si \rightleftharpoons$ Si + W is completed, and at the bottom by two eutectic lines: Si + W + Al and Si + $CuAl_2$ + W.

The region of secondary crystallization of Si + $CuAl_2$ is bounded at the bottom by two eutectic lines of tertiary crystallization: Si + $CuAl_2$ + W, and Si + $CuAl_2$ + Al.

The two horizontals on the cross section represent the following nonvariant equilibria:

$$\text{Liq.} + Mg_2Si \rightleftharpoons Si + Al + W \text{ and}$$

$$\text{Liq.} \rightleftharpoons Si + Al + W + CuAl_2.$$

SUMMARY

1. The structural diagram of the Al -Cu - Mg - Si system has been constructed from the physico-chemical analysis by thermal and microscopic methods, of nine linear cross sections of its tetrahedron.

2. Six nonvariant equilibria have been found at the aluminum vertex of the system:

1. Liq. $\rightleftharpoons$ Al + Mg_2Si + T + Al_3Mg_2 at 444°

2. Liq. $\rightleftharpoons$ Al + Mg_2Si + $CuAl_2$ + S at 500°

3. Liq. $\rightleftharpoons$ Al + Si + $CuAl_2$ + W at 505°

4. Liq. + S $\rightleftharpoons$ Al + Mg_2Si + T at 464°

5. Liq. + Mg_2Si $\rightleftharpoons$ Al + $CuAl_2$ + W at 510°

6. Liq. + Mg_2Si $\rightleftharpoons$ Al + Si + W at 521°

corresponding to six secondary tetrahedra formed at the aluminum vertex of the system.

The nonvariant points corresponding to the 1st, 2nd, and 4th equilibria are close in their compositions to those of the corresponding nonvariant points of the ternary system Al - Cu - Mg and closely adjoin the Al - Cu - Mg face of the tetrahedron, their distance from the face being 0.3 to 0.45% Si. The temperatures corresponding to these nonvariant points are practically identical with the temperatures of the ternary points in the Al - Cu - Mg system, their difference being of the order of 1-2°.

The three other nonvariant points are also generally shifted toward the Al - Cu - Mg face of the tetrahedron.

3. The quaternary phase W found in the system, with the approximate composition of $Al_xCu_4Mg_5Si_4$, is formed from Mg_2Si by a peritectic reaction.

Accordingly, its composition lies outside the region of its primary crystallization.

4. The results of our research indicate that when alloys at the aluminum vertex of the Al - Cu - Mg - Si system are investigated, allowance must be made not only for the presence of the phases that exist in the Al - Cu - Mg, Al - Mg - Si, and Al - Cu - Si ternary systems, but also for the existence of the quaternary phase W.

The authors wish to express their profound gratitude to Academician G.G.Urazov for his valuable counsel and instructions during the performance of this research and for his unflagging interest.

LITERATURE CITED

[1] G.G.Urazov and D.A.Petrov, J. Phys. Chem., Nos. 4-5 (1946).

[2] H. Nishimura, Chem. Col. Engng. Kyoto, 10, 18 (1937).

[3] R. Vogel, Z. allg. anorg. Ch., 107, 265 (1919).

[4] Janecke, Kurzgefasstes Handbuch aller Legierungen (1937).

[5] V. Fuss, Z. Metall., 16, 24 (1924).

[6] A.G.C.Gwyer, H.W.L Phillips, L. Mann, J. Inst. Metal, 40, 297,(1928).

[7] G.G.Urazov, S.A.Pogodin, and G.M Zamoruyev, Izvest. Inst. Phys. Chem. Analysis, 5, 157 (1931).

[8] D.Hanson, M.L.V.Gayler, J.Inst. Metal., 26, 321 (1921).

[9] M.L.V.Gayler, J. Inst. Metal., 30, 139 (1923).

[10] F Laves,H.Witte, Metallwirtsch., 15, 15 (1936).

[11] E.H.Dix, G.F.Sager, B.P.Sager, Am. Inst. Mining Met. Engrs., Tech. Pub. 99, 119 (1932).

[12] D.A.Petrov, J. Phys. Chem., 9, 522 (1937); D.A.Petrov, Acta Phys. Chem. USSR, 6, 505 (1937).

[13] D.A.Petrov, J. Phys. Chem., 10, 1161 (1946).

Received September 20, 1947.

ALUMINA FOR CHROMATOGRAPHIC ADSORPTION AND A CHARACTERIZATION OF ITS ACTIVITY

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I

In recent years chromatographic adsorption has been more and more widely employed in the purification and separation of mixtures of different substances.

This is indicated by the employment of chromatography in numerous research projects on glucosides, alkaloids, antibiotics, vitamins, hormones, and the like, as well as by its use in projects devoted to research on the process of chromatographic adsorption itself.

Worthy of first mention is the monograph by the founder of chromatographic adsorption M.S.Tsvet. [1], which is the classic work in this field. Then there are several survey articles [2] and monographs, in addition to a large number of papers dealing with research into the mechanism of the phenomenon of chromatographic adsorption [3].

Substances of the most diversified class of compounds are employed as sorbents for chromatography (cf the literature cited above). The most widely used, however, is alumina.

The paper by Brockmann and Schodder [4] describes the method of preparing chromatographic alumina of varying activity. According to Brockmann, however, the conditions for performing these operations are so indefinite that they cannot ensure the production of the desired reproducible results. That is why we undertook the development of a method of preparing chromatographic alumina of differing degrees of activity and provided a characterization therof.

II

If we start with aluminum hydroxide, the entire process of preparing a chromatographic alumina consists of three stages: the first stage involves the grinding of the initial hydroxide and then screening it to obtain a homogeneous powder of the requisite fineness. Then this powder is subjected to heat treatment at a suitable temperature to provide a sorbent of maximum activity. Finally, the active alumina is dampened in one way or another to produce a sorbent whose activity has been reduced to the extent desired.

In the present research our initial material was the so-called "catalytic alumina," employed to dehydrate alcohol in the synthesis of ethylene. According to analysis performed in the analytical section of the All-Union Research Institute of Pharmaceutical Chemistry, samples of this material procured at different times possessed 2.7 to 4.8% moisture (determined by drying at 110° until constant weight was reached) and 0.002 to 0.01% of heavy metals.

The large pieces were crushed in a porcelain mortar, after which the product was passed through the following silk screens: Nos. 29, 50, and 60.* This yielded 3 fractions, characterized by the following grain size, measured under the microscope:

Fraction 1 .....0.196 mm
Fraction 2.....0.097 mm
Fraction 3.....0.044 mm.

The measurements were made with an ocular micrometer. They indicated that the powder was fairly homogeneous within the limits of each fraction.

III

As we know, alumina can be obtained in various modifications. According to the literature, the highest activity is manifested by γ-Al_2O_3, which is prepared by dehydrating precipitated $Al(OH)_3$ in a vacuum at 600°.

Other authors, however, subjected alumina to treatment at lower temperatures, namely, 300-400°, in preparing it for use in chromatographic adsorption. In the paper by Brockmann and Schodder [4] the temperature is not stated at all.

After several preliminary tests at various temperatures, we settled on the temperature of 300° for activation.

The powder was placed in a layer 5 mm thick in an aluminum tray, placed in a muffle furnace. The temperature of the furnace was first raised to 300°, and then not allowed to vary from that temperature by more than ±5° for three hours. After activation was complete, the tray with its powder was transferred to a phosphorus=pentoxide exsiccator. The activated alumina was stored in bottles with paraffined stoppers.

IV

Numerous research papers in which chromatographic adsorption is used refer to one or another activity group of the alumina used, as measured by Brockmann. Brockmann and Schodder, in their paper [4], describe their method of preparing aluminum oxide of various degrees of activity. This method entails leaving the alumina, after heat treatment, in open pans to be dampened by atmospheric moisture.

It is evident that it is extremely difficult to produce a high-quality sorbent of the requisite activity in this way.

Nor can the method of deactivation proposed in a British patent [5] guarantee the production of a sorbent of homogeneous activity. According to this patent, 1 to 10% of water is added to the activated alumina after it has cooled, followed by stirring until a homogeneous deactivated mass is obtained.

The need was therefore apparent for the development of a method for the deactivation of alumina that would ensure the attainment of reproducible results. The essential conditions for this are:

1) Deactivating the alumina within a closed space at constant air moisture.

2) Careful stirring of the powder during deactivation.

We designed an apparatus that ensures the production of a sorbent with a high degree of homogeneity as far as activity is concerned and with satisfactory reproducibility of our experimental results.

The apparatus, shown schematically in Fig. 1, consists of a drum 1,

*The screen number denotes the number of holes per running centimeter.

revolving at a fixed speed on shaft 2, within the housing 3, which is closed by the cover 4. A small amount of water is poured into the bottom of the housing, the water temperature, which is kept constant, being measured by the thermometer 5. The drum has round holes 6 in both ends. Fixed vanes 7 that are perforated

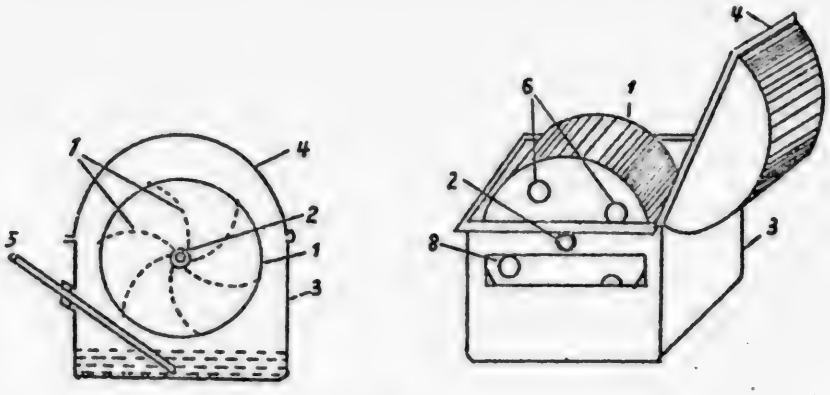

Fig. 1

all over their surface are attached to the inside wall of the drum. The alumina to be moistened is charged into the drum, and as the latter rotates within the closed housing, the alumina spills from one vane to another through the holes in the vanes, being moistened as it does so by the water vapor that saturates all the air in the housing. Glass windows 8 are fitted into the two end walls of the housing, parallel to the ends of the drum, to facilitate observation of the apparatus's operation. The apparatus is made of tinned copper.

In our tests 25 ml of activated sorbent (Fraction 2) was charged into the drum. The temperature of the water inside the housing was kept at 20° (± 1°). Samples of the sorbent were taken from the apparatus at fixed intervals to be tested chromatographically and to have their moisture content determined.

Table 1

Duration of moistening, min.	Moisture content, percent
15	0.7
30	2.42
45	3.64
60	4.9
75	6.1
90	6.75
105	7.83
120	8.62
135	10.4
150	11.4

Moisture was determined by drying the sample at 105-110° until constant weight was reached.

The results of moisture determinations of the samples as a function of the moistening time are listed in Table 1. These are the results of 8 tests of varying duration. Two samples were taken from each of two successive tests, the duration being the same for the two samples. The discrepancy between the two samples did not exceed 0.5% moisture content.

These results are presented graphically in Fig. 2. As the graph indicates, the variation of the amount of water adsorbed by the alumina with the moistening time is represented by a straight line under the conditions of our experiment, within the range of the moisture content

achieved: up to 12%. The maximum deviation of the individual points from the straight line (two instances) is 5%.

In addition to the mositure-content determination, the moistened samples of alumina were tested chromatographically by the Brockmann method.

This was done by preparing solutions of two dyes in the combinations set forth in Table 2. 0.04 g of each dye was taken per 100 ml of solution. A 1:4 mixture of benzene and gasoline was used as the solvent.

We procured the dyes from the Pigment and Dye Research Institute. Each of them was tested for the absence of any foreign impurities by dissolving it in the foregoing solvent and then passing it through the column with the alumina of the corresponding activity. These tests showed that the dyes used by us were free of all foreign impurities.

The benzene, subjected to preliminary desiccation over calcium chloride, was then distilled into a column. The fraction with a b.p. of 80° was used in our tests.

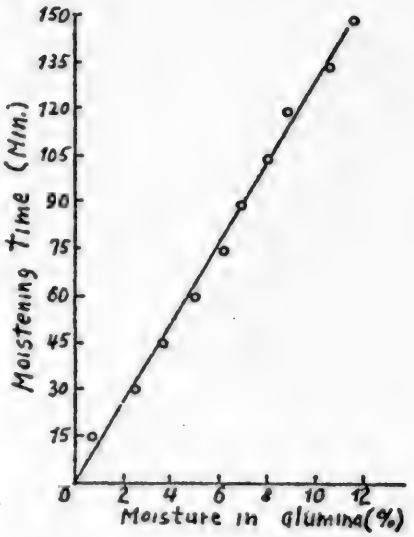

Fig. 2

The gasoline had a b.p. range of 50-140° after analogous treatment.

The performance of chromatographic tests is fully described in the literature; various authors have modified the process to fit the sorbents they used and the substances they were investigating.

TABLE 2

Brockmann activity group	Dye and its location in the alumina column
1	Methoxyazobenzene (top) Azo benzene
2	Sudan Yellow (top) Methoxyazobenzene
3	Sudan Red (top) Sudan Yellow
4	Aminoazobenzene (top) Sudan Red
5	Hydroxyazobenzene (top) Aminoazobenzene

We performed these tests as follows in the present research project.

A tube 18 mm in diameter and 250 mm long, drawn out at one end, is attached through rubber tubing to a vessel fitted with a side drain. The bottom of the wide part of the tube is filled with absorbent cotton, the upper part being filled with filter paper. Then alumina (Fraction 2) is poured into the tube, while the sides of the latter are continuously tapped, until it forms a layer 50 mm high. Special tests have shown that when the column is filled in this manner, it is densely packed, and that pressing down on the packing with a wooden rod does not increase the density of this sorbent any further. A circle of filter paper is placed on the surface of the sorbent.

The column prepared in this manner is wetted with the solvent (benzene + gasoline), which is poured into the tube in small batches at a time. Then a dropping funnel containing 5 ml of the dye solution is placed in the top of the tube in such a fashion that the lower end of the funnel stem is about 5 mm from the sorbent layer. Adding the solution is begun when the layer of solvent in the tube is less than 1 mm. The solution is added evenly, a drop at a time, so as to keep its level constant. A series of tests convinced us that these conditions were indispensable to obtain reproducible and comparable results.

After all the solution has passed through the column, colored zones form in the upper section of the column, but the demarcations between the colors are not distinct enough. These zones are "developed" to attain clearer demarcation between them; this consists in passing the solvent (gasoline + benzene) through the column.

After development is complete, the receiver is connected to a water-jet pump, and air is sucked through the column for some time at low speed, after which the test is considered over.

Table 3 gives the results of our chromatographic tests of the alumina moistened in our apparatus to various degrees of moistness.

TABLE 3

Sample moisture content, %	Dye solution	Zones (from top to bottom)		Remarks
		Color	zone width mm	
0	III	Dirty Bordeaux	4	No separation
5.3	III	Violet	6	Distinct separation
		Rose-yellow ...	6	
6.3	III	White	1	
		Violet.....	6	Sharp separation
		Rose-yellow....	6	
7	III	White.....	3	
		Violet.....	13	Zones diffused
		Rose-yellow	8	
7	IV	Yellow.....	4	Distinct separation
		Violet.....	8	
7.7	IV	White.....	2	
		Yellow.....	5	Sharp separation
		Violet.....	13	
10	V	Bright yellow .	3	
		White.....	2	Sharp separation
		Pale yellow ...	9	
11.5	V	Bright yellow .	5	
		White	7	Sharp separation
		Pale yellow ...	9	

If we take the moisture content of the alumina of the 3rd activity group as 5.5 $\pm$ 0.5%, that of the 4th group as 7.5 $\pm$ 0.5%, and that of the 5th group as 9.5 $\pm$ 0.5%, the graph of the variation of sample activity with moisture content is a straight line, as shown in Fig. 3. If we assume that this function is linear throughout the activity range, we can establish the moisture that the alumina of the first two activity groups must have with an accuracy that suffices

for this procedure (we were unable to establish these values by color separation owing to the unavailability of methoxyazobenzene). Our results, experimental as well as those obtained by graphical extrapolation, are listed in Table 4.

It is a matter of course that the foregoing method can be used to prepare alumina of any desired activity, in between any two groups, as well as an alumina whose activity extends beyond the limits of this series.

TABLE 4

Sample moisture content, %	Brockmann activity group
2	1 (extrapolated)
3.8	2 (extrapolated)
5.5	3
7.5	4
9.5	5

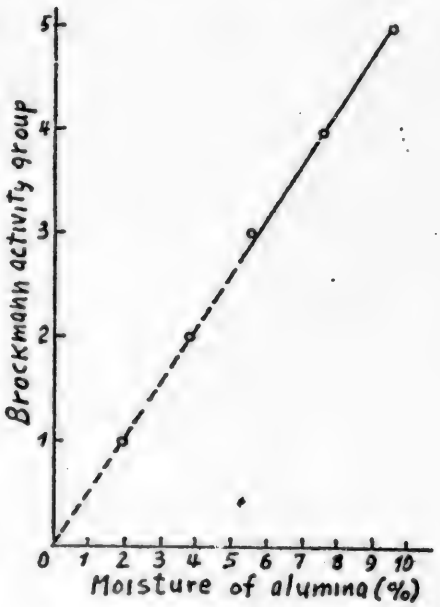

Fig. 3

SUMMARY

1. A method has been developed for producing chromatographic alumina of varying degrees of activity, corresponding to the Brockmann activity groups. This method, which consists of moistening the alumina in an apparatus of special design, ensures the production of a sorbent with a high degree of homogeneity as far as activity is concerned, together with satisfactory reproducibility of results.

2. It has been shown that the activity of the sorbent produced by this method can be found by simply determining its moisture content instead of the comparatively complicated Brockmann method of determining its activity group by means of dyes, which are not available everywhere.

LITERATURE CITED

[1] M.S.Tvset. Chromatographic Adsorption Analysis. Publishing House of the USSR Academy of Sciences (1946).

[2] N.A.Fuks, Distributive chromatography and its use in analytical chemistry, Prog. Chem, USSR, 17, No. 1, p. 45 (1948); E.N.Gapon and T.B.Gapon, Chromatographic analysis of ions, Prog. Chem., 17, No. 4, p 452 (1948); M.M. Senyavin, Chromatographic adsorption analysis, Prog. Chem., 18, No. 2, p. 183 (1949); N.A.Fuks, Achievements of the method of chromatographic analysis in organic chemistry, Prog. Chem., 18, No. 2, p 206 (1949).

[3] E.N.Gapon and T.B.Gapon, Doklady Akad. Sci., USSR, New Series, 59, 921 (1948); E.N.Gapon, Doklady. Akad. Sci. USSR, New Series, 60, 817 (1948); Wilson, J. Am. Chem. Soc., 62, 1583 (1940); Weill-Malherbe, J. Chem. Soc., 1943, 305; Weiss, J. Chem. Soc., 1943, 297.

[4] Brockmann, Schodder, Ber., 74, 73 (1941).

[5] Brit. Patent No. 566405.

Received May 31, 1948.

POLAROGRAPHIC INVESTIGATION OF COORDINATION COMPOUNDS OF ZINC AND HYDROXYL

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The action of alkalies upon zinc hydroxide is accompanied by the entrance of the precipitate into solution and the formation of complex anions of varying composition. In some cases the salts that correspond to these anions have been isolated in the pure state.

Stachelberg and Freyhold used the polarographic research method to determine the composition of the complex anion [1]. These authors found a relationship between the wave potential of zinc reduction and the concentration of sodium hydroxide in solution ranging from 0.1N to 4.0N. They used a 0.1N solution of potassium nitrate as the auxiliary indifferent electrolyte. The coordination number of the complex anion was found to be 4, and the instability constant was found to be $1.3 \cdot 10^{-17}$.

As these authors investigated this reduction over an extremely wide range of alkali concentrations and at intervals of 0.5 N, it seemed to us to be desirable to try to confirm the presence of complex anions of other compositions in the solution. There is no doubt that equilibrium is set up between the complex anions formed and the free hydroxyl ions, the position of this equilibrium shifting to one side or the other, depending on the alkali concentration. It is quite possible for complex anions of zinc, with a smaller percentage of hydroxyl ions, to be formed in solutions that are comparatively poor in hydroxyl ions, and, conversely, the composition of the complex anion may be more complicated at high alkali concentrations.

We investigated the reduction of zinc from a solution of its sulfate in the presence of 0.01N sodium sulfate and of various quantities of sodium hydroxide. The alkali concentration was varied from 0.2N to 2.0N in steps of 0.1N to 0.2N. The zinc concentration was taken as 0.001N. In every test, the dissolved oxygen was blown out by a current of hydrogen. Reduction of zinc from alkaline solutions of higher concentration than 2.0N indicated that in this case the zinc waves grow smaller, and, moreover, have a quite truncated top, which makes it impossible to measure the half-wave potential of reduction with any degree of accuracy. In these solutions, the equation of the polarographic wave:

$$\Pi = \Pi_{1/2} - \frac{2.3\,RT}{nF} \lg \frac{i}{i_d - i}, \qquad (1)$$

does not hold good, apparently because of the irreversibility of the process of reducing zinc from the coordination compound and the slow dissociation of the latter.

Our measurements were made at temperatures of 0, 20, and 30° ($\pm$ 0.1°) with a mercury drop electrode of usual design.

A saturated calomel electrode was used as the anode, connected to the

electrolyzer through an intermediate solution by means of an agar-agar bridge with potassium chloride. A visual device, enabling us to compute the current directly on the galvanometer scale was used to plot the polarogram. The cathode potential was measured to the nearest millivolt by a compensation method.

We were able to establish that a linear relationship exists between the half-wave potential and the logarithm of the activity of the hydroxyl ions, described by the following equations:

$$(\Pi_{1/2})_k = -\Pi' - 0.09 \lg a_{OH^-} \qquad (2)$$

at all three temperatures for alkali concentrations from 0.1N to 1N, with Π' = 1.455 for 0°, 1.460 for 20°, and 1.463 for 30°; and by

$$(\Pi_{1/2})_k = -\Pi'' - 0.12 \lg a_{OH^-} \qquad (3)$$

for sodium hydroxide concentrations of 1.1N to 2.0N, where Π' = 1.457 for 0°, 1.462 for 20°, and 1.466 for 30°.

When we compare these equations with the expression for the shift of the half-wave potential in the formation of a coordination compound [2]:

$$\frac{d(\Pi_{1/2})_k}{d\lg a_{OH^-}} = -p \cdot 2.3 \frac{RT}{nF}, \qquad (4)$$

we see that the coordination number of the coordination compound is 3 and 4 for the limits of alkali concentration specified above.

Thus the composition of the coordination compound in the solution depends on the alkali concentration, the composition of the inner sphere of the complex anion growing more complicated as the alkali concentration rises.

At an alkali concentration of about 1.1N, the concentrations of both forms are commensurable, and the coefficient of the logarithmic term of Equations (2) and (3) changes from 0.09 to 0.12.

To find the instability constant of coordination compounds of zinc with hydroxyl ions we employed the equation for the shift of the half-wave potential during the formation of coordination compounds [2]:

$$(\Pi_{1/2})_k - (\Pi_{1/2})_2 = \frac{2.3RT}{nF} \lg k_c - p \cdot 2.3 \frac{RT}{nF} \lg a_{OH^-} \qquad (5)$$

$(\Pi_{1/2})_2$, the half-wave potential of zinc reduction from a solution containing sodium sulfate, was measured by us and found to be 1.00 volt. With this value and Equations (2) and (3) we calculated the instability constants of coordination compounds with coordination numbers 3 and 4 at temperatures of 0, 20, and 30°. The results of this calculation are listed in the table.

Instability Constants of Coordination Compounds of Zinc and Hydroxyl at Various Temperatures

p \ T°	0	20	30
3.....	$1.45 \cdot 10^{-17}$	$1.38 \cdot 10^{-16}$	$3.54 \cdot 10^{-16}$
4.....	$1.23 \cdot 10^{-17}$	$1.12 \cdot 10^{-16}$	$2.82 \cdot 10^{-16}$

The table shows that the stability of the complex anion rises somewhat as the coordination number is increased. Rising temperature lowers the stability of the complex ions, however. The change in the instability constant with temperature made it possible to determine the heat of formation of the complex anion of zinc and hydroxyl. As the temperature limit is not very high, and there are only three values of the constant for different temperatures, calculation of the heat of formation yields only an approximate value, 18,000 cal per mole of the coordination compound formed.

SUMMARY

1. The reduction of zinc from solutions containing hydroxyl ions was investigated; it was found that complex ions with coordination numbers 3 and 4 are formed.

2. The instability constants of the coordination compounds are of the order of 10^{-16} to 10^{-17} and vary with the solution temperature.

3. An approximate value of the heat of formation of the complex anions, 18,000 cal per mole, was computed from the temperature variation of the stability constants of the coordination compounds.

LITERATURE CITED

[1] M. Stachelberg and H. Freyhold, Z. Electrochem., 46, 120 (1940).

[2] Y. Geirovsky. The Polarographic Method of Analysis. United Technological Publishers (1937).

Received July 1, 1948.

RESEARCH ON GALVANIC CIRCUITS IN TOLUENE

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In our preceding paper [1] we described our research on the electromotive forces in benzene solutions of $AlBr_3$ to which the halides of various metals had been added.

In the present paper we report on analogous research on toluene solutions. The method of measurement was somewhat different from that employed earlier. Formerly, we used the customary method of eliminating or reducing the diffusion potential by means of the so-called intermediate electrolyte. Inasmuch as a series of preliminary tests had shown that the value of the e.m.f. remains almost unchanged in the medium under investigation if no intermediate electrolyte is used, we also made a series of tests without an intermediate electrolyte. Eliminating the intermediate electrolyte is desirable, owing to the high resistance of the solution caused by the electrolyte, which makes it hard to measure the e.m.f.

In the present research we made a series of tests to investigate the electrode potential of such metals as aluminum, bismuth, silver, antimony, copper, and arsenic.

The feasibility of measuring electrode potentials in toluene was settled by a number of papers by V.A.Plotnikov and his associates [3] on the conductivity and the decomposition potentials of toluene solutions of aluminum bromide when halides of the foregoing metals are added to the solution.

A solution of $AlBr_3$ in toluene is almost a non-conductor, but silver, copper, bismuth, antimony, and arsenic bromides are readily soluble in this solution, which then becomes a conductor.

When toluene solutions of $AlBr_3 - KBr$, $AlBr_3 - AgBr$, $AlBr_3 - CuBr$, $AlBr_3 - Sb - Br_3$, and $AlBr_3 - BiBr_3$ are electrolyzed, Al, Ag, Cu, Sb, and Bi are deposited, respectively at the cathode, in accordance with the data in the literature.

Measurements of the decomposition potentials in the foregoing binary systems of salts in benzene and toluene solutions indicate that in many cases the decomposition potentials in toluene solutions are different from those in benzene solutions.

EXPERIMENTAL METHODS AND RESULTS OF MEASUREMENT

The toluene was purified by shaking it up with sulfuric acid. The toluene was then separated from the sulfuric acid and washed free of acid, first with a solution of NaOH and then with water; after the water had been removed, the toluene was desiccated with metallic sodium. The desiccated toluene was then distilled over metallic sodium. The product was redistilled at a fixed temperature and then sealed in ampoules. The purification of the salts used (with the sole exception of the $AsBr_3$) was described in the preceding paper. Chemically

pure arsenic bromide was distilled and sealed into ampoules. For our tests we used a preparation that was completely colorless and had been refined by double distillation. Rods of solid cast metal or electrolytically deposited metals were used as the electrodes. The silver electrode was prepared by depositing silver electrolytically upon a silver wire in a cyanide bath.

The aluminum electrode was a thin plate of chemically pure sheet aluminum. The copper electrode was a wire of chemically pure copper.

The bismuth and antimony electrodes were rods of cast metal. The arsenic electrode was prepared by depositing arsenic electrolytically from a 10% solution of $AsBr_3$ in ether.

In all our tests the solvent used was a solution of aluminum bromide in toluene, with an $\frac{AlBr_3}{toluene}$ ratio of 0.25. This solution was prepared immediately before the beginning of a run, owing to the undesirability of keeping it for any length of time (possible hydrolysis). Then the requisite amount of halide of the metal whose potential was to be determined was poured into a small flask containing the solvent.

The weight of metallic halide was so chosen as to make the $\frac{MeHal}{AlBr_3}$ ratio equal 0.1

The comparison electrode used, as in the previous paper, was silver, immersed in a standard electrolyte, i.e., a solution whose $\frac{AgBr}{AlBr_3}$ ratio equaled 0.1.

This electrode was freshly prepared anew for each circuit.

As the stability of the e.m.f. in such media is less than in aqueous solutions, the tests with each galvanic circuit were repeated several times until the results corresponded closely.

The initial value of the e.m.f. was measured 15 minutes after the cell had been set up; it took an hour for the value of the e.m.f. to become steady. In some cases this value of the e.m.f. remained unchanged for twenty-four hours. this was the case for Cu and Bi. The Al, As, and Sb potentials were less steady, the precision of measurement of these potentials not exceeding a hundredth of a volt.

Upon standing, some solutions resinified, separating into layers, probably because of the formation of a Gustavson coordination compound.

The slow establishment of the potential may be due to the slow rate of formation of the coordination compound. The slow rate of formation of the coordination compound in the $AlBr_3 - AsBr_3$ system was established by Plotnikov and Yakobson [3], who observed the change in conductivity with time.

In the more stable systems, with copper and bismuth bromides, the deviations in individual e.m.f. measurements did not exceed 1 to 2 millivolts.

A summary table of the e.m.f's in the investigated circuits is given below:

$$\text{Me} \;\Big|\; \frac{AlBr_3}{\text{toluene}} = 0.25,\ \frac{MeHal}{AlBr_3} = 0.1 \;\Big\|\; \frac{AlBr_3}{\text{toluene}} = 0.25,\ \frac{AgBr}{AlBr_3} = 0.1 \;\Big|\; \text{Ag}$$

The potential of the silver electrode is taken as zero.

As seen in the table, the potential sequence of the metals investigated

has a quite different order from that of the normal potentials of the same metals in aqueous solutions.

Whereas in water the sequence of normal potentials is as follows: Al, Bi, Sb, As, Cu, Ag, the potential sequence in the $AlBr_3$ – MeBr – toluene system is as follows: Al, Cu, Ag, Bi, Sb, As.

The shift of silver in the potential sequence is found in both the benzene and toluene solutions. This shift of silver in the potential sequence was also found by Izbekov [4], who used fused $AlBr_3$ as his solvent.

Electrode	Electrode potential, volts		Sequence of normal potentials in aqueous solution, taking the potential of silver as zero.
	In a toluene solution of $AlBr_3$ - MeHal	In a benzene solution of $AlBr_3$ - MeHal	
Al/Al^{+++}	-0.075	-0.306	-2.728
Cu/Cu^{+}	-0.026	-0.023	-0.268
Ag/Ag^{+}	0.000	-0.000	0.000
Bi/Bi^{+++}	+0.309	+0.393	-0.608
Sb/Sb^{+++}	+0.470	+0.497	-0.608
As/As^{+++}	+0.590	–	-0.508

The order of potentials established by measuring the e.m.f. was confirmed by experiments on the direct displacement of the metals. Though the sequence is the same in the potential series for benzene and toluene solutions, the absolute magnitudes of the electrode potentials differ.

The greatest difference is found in the potential of aluminum, which may be related, evidently, to the different values of the decomposition potential of $AlBr_3$ – KBr in benzene and toluene solutions, as established in the research done by Plotnikov and his associates.

We find that the two values almost coincide for copper, with only a slight difference being observed, toward a lowering of the potential, in the cases of bismuth and antimony.

For the sake of comparison, we cite below the series of potentials found by other authors in their work on various nonaqueous media:

Pyridine: Al, Cu, Sb, Bi, Hg, Ag (Kahlenberg [5]).
Acetone: Zn, Cd, Co, Bi, Hg, Cu (Skobets [6]).
Fused $AlBr_3$: Al, Zn, Cd, Ag, Hg, Sb, Bi (Izbekov [4]).

Hence, it may be stated that the considerable formation of coordination compounds in these media greatly affects the sequence of the potentials of the metals investigated.

SUMMARY

1. Research has been done on the e.m.f. of galvinic circuits in these toluene solutions: $AlBr_3$-AgBr, $AlBr_3$ - KBr, $AlBr_3$ - CuBr, $AlBr_3$ - $SbBr_3$, $AlBr_3$ - $BiBr_3$, $AlBr_3$ - $AsBr_3$.

2. Measurements were made of the following metals: Al, Bi, Cu, Sb, and As, paired with a silver electrode.

3. The sequence of potentials for these metals is arranged in the following order: Al, Cu, Ag, Bi, Sb, As.

4. This potential sequence differs from that of the same metals in aqueous solutions, but coincides with the sequence found in benzene solutions.

LITERATURE CITED

[1] V.S.Galinker and I.L.Katsnelson, J. Gen. Chem., USSR, 15, 9-10, 711 (1945).

[2] I.L.Katsnelson, S.I.Yakubson, Rep. Inst. Chem. Ukr. Acad. Sci., V, 4, 387 (1938).

[3] V.A.Plotnikov and S.I.Yakubson, J. Phys. Chem., 8, 159 (1936).

[4] V.A.Izbekov, Z. Phys. Chem., 116, 385 (1905).

[5] Kahlenberg, Z. Electroch., 11, 385 (1905).

[6] E.M.Skobets, Rep. Inst. Chem. Ukr. Acad. Sci., V, 2, 176 (1938).

Received July 2, 1948.

HOMOLOGUES OF MONOVINYLACETYLENE

I. β-Tert-BUTYLVINYLACETYLENE

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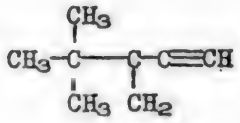
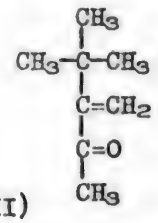
The first member of the homologous series of hydrocarbons with the general formula C_nH_{2n-4} is monovinylacetylene. Monovinylacetylene possesses all the properties of monosubstituted acetylenic hydrocarbons. All known substituted homologues of monovinylacetylene, in accordance with the properties of monosubstituted acetylenes, yield a characteristic precipitate with an ammoniacal solution of cuprous oxide; negligible traces of isopropenylacetylene, for example, yield a precipitate with Iloswey's reagent [1]. Grignard isolated a copper derivative of 6-methylene-3-heptyne-1 [2]. On the basis of our previous research paper [3] we established that β-tert-butyl-vinylacetylene does not form a precipitate with Iloswey's reagent, despite the presence of free acetylenic hydrogen in it. In oxidizing the hydrocarbon we identified trimethylpyruvic acid with good yield as its p-nitrophenylhydrazone; this justifies our assigning the structure of 4,4'-dimethyl-3-methenepentyne-1 to this synthesized hydrocarbon (I):



(I)

The present research was undertaken to ascertain the ability of β-tert-butylvinylacetylene to form a sodium derivative and its ability to enter into a hydration reaction.

The hydrocarbon was hydrated by the method developed by Churbakov [4] for monovinylacetylene; according to K. A. Oglobin [5], who effected the hydration of isopropenylacetylene under the same conditions, the yield of the ketone was 78%. We succeeded in synthesizing the ketone under the conditions specified by the foregoing authors, but the ketone yield was only 50%:



(II)

4,4'-Dimethyl-3-methenepentanone-2

We synthesized the sodium derivative of β-tert-butylvinylacetylene by reacting finely divided sodium with the hydrocarbon. We used the sodium derivative later to synthesize β-tert-butylvinylacetylenecarboxylic acid and its ethyl ester.

There is not much in the literature on acids containing double and triple bonds. Carothers [6] described the synthesis of vinylpropiolic acid by the action of carbon dioxide on vinylacetylenemagnesium bromide at 0°. This acid proved to be extremely unstable, rapidly darkening and polymerizing upon standing. It decomposes explosively when heated to 110°. Owing to these properties, Carothers was unable to obtain it in pure form. The author made no effort to synthesize and isolate esters of this acid. I.N.Nazorov [7] synthesized vinylpropiolic and isopropenylpropiolic acids:

$$CH_2=CH-C\equiv C-COOH; \qquad CH_2=\overset{CH_3}{\underset{|}{C}}-C\equiv C-COOH.$$

In synthesizing these acids the authors started out with monovinylacetylene and isopropenylacetylene. The corresponding sodium derivatives were obtained by reacting sodium amide with the hydrocarbon; these derivatives were then converted into the acids by saturating them with anhydrous carbon dioxide. Both acids proved to be unstable toward oxygen; they were not obtained in the pure state.

The acids were esterified by the usual methods, forming more stable esters that distilled in vacuum without decomposition. The esters are colorless mobile liquids possessing an extremely acrid odor that were very lachrymatory. The German patent issued to Charles Moureu [8] states that the methyl ester of 2-methyl-heptene-2-yne-6-carboxylic acid

$$(CH_3)_2C=CH-CH_2-CH_2-C\equiv C-COOCH_3$$

is a valuable substance for the perfumery industry. When added to synthetic fragrances, it gives them the odor of natural flowers.

We see, therefore, that whereas the esters of the lower acids have an extremely unpleasant odor, the esters of higher acids are valuable in perfumery. It was of interest to investigate the properties of the ester of β-tert-butylvinylacetylenecarboxylic acid in this connection.

Little research has been done on the odors of aliphatic compounds with a triple bond in the carbon chain. Not even for the well-known esters of heptynecarboxylic acid is there any information of the effect of the position of the triple bond in the carbon chain upon the odor. Our first task in synthesizing β-tert-butylvinylacetylenecarboxylic acid was the synthesis of the sodium derivative of the hydrocarbon.

There are references in the literature to various ways of obtaining sodium derivatives of the higher homologues of monosubstituted acetylenic hydrocarbons. We shall briefly touch upon only four examples, which involve the synthesis of metal derivatives, starting with the respective hydrocarbon and sodium. Moureu [9] gives the following prescription for synthesizing the sodium derivative of enanthylidene: to finely divided sodium there is added enanthylidene that has been diluted with 5 times its weight of ether. The reaction of forming the sodium derivative (the acetylide) is exothermic, and the ether starts to boil. According to the author's instructions, however, it is impossible to effect a complete reaction between the sodium and the hydrocarbon, owing to the coating of the particles of unreacted metal with a crust of the acetylide. As a result, the author later synthesized the sodium derivative by the action of heptyne upon sodium amide in vaseline oil.

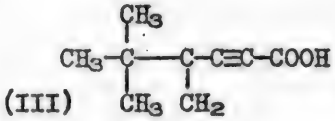
S. Nametkin and V. Isagulyants [10] evolved a method for the synthesis of heptyne carboxylic acid from heptynesodium. We tried out several methods to synthesize our sodium derivative.

The finely divided sodium was obtained by agitating it in toluene that

had been brought to the boiling point. The toluene was decanted off, and the sodium was covered with a layer of absolute ether. The hydrocarbon, diluted with twice its weight of ether, was then poured into the flask. Only a small amount of the metal derivative was seen to form.

The derivative yield was negligible, even when the reaction was effected in an ether-toluene medium. Since it was difficult to achieve a complete reaction between the hydrocarbon and the sodium because of the coating of the metal with a layer of the acetylide, the yield of the latter largely depends upon the fineness to which the sodium has been divided. Extremely active, finely divided sodium was obtained by shaking up the fused metal under xylene. The reaction to form the sodium derivative was effected in xylene. When this was done, we were able to bring the reaction to completion. It is best to effect the reaction of sodium with the hydrocarbon and the subsequent carbonization in ether, since the highly unsaturated acid polymerizes and resinifies when a high-boiling solvent is driven off.

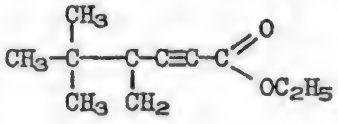
Although we effected the synthesis of the sodium derivative and its carbonization in xylene, we were able to avoid heating the acid when separating it from the reaction mass as follows: After the sodium derivative had been saturated in the xylene with carbon dioxide, the sodium salt of the acid was extracted with a few batches of water. The aqueous extracts are almost colorless, all the resinification products remaining in the xylene. The aqueous solution of the salt was acidulated with sulfuric acid, and the acid was extracted. We thus succeeded in synthesizing a nearly colorless acid, that was free of resinification products (III).



(III)

β-Tert-butylvinylacetylenecarboxylic acid
(2,2'-Dimethyl-3-methene-4-hexyne-6 acid)

The acid is a thick liquid that rapidly darkens and polymerizes when exposed to the air. The silver salt of the acid was synthesized. The ethyl ester of the acid was synthesized by reacting the sodium derivative of the hydrocarbon with ethyl chlorocarbonate (IV).



(IV)

The ester has a pleasant apple odor. It is more stable than the acid, but it still grows cloudy and polymerizes upon standing.

EXPERIMENTAL

Hydration of β-Tert-butylvinylacetylene

This hydration was effected in accordance with the instruction given by Churbakov [4] for monovinylacetylene.

In a flask fitted with a stirrer and a reflux condenser there was placed 30 g of the hydrocarbon, 8.4 g of mercuric oxide, 23 ml of sulfuric acid, 520 ml

of water, and 60 ml of a 50% solution of ferric sulfate. The reaction mass was heated to 80° for 4.5 hours. The synthesized ketone was driven off with steam and extracted with ether. The ether extract was desiccated with calcium chloride. After the ether had been driven off, the product was distilled in vacuum. The yield of the ketone was 50% of theory.

B.p. 80-81° at 110 mm: d_4^0 0.8622; $d_4^{17.5}$ 0.8492; $n_\alpha^{17.5}$ 1.43650; MR_α 39.10.
$C_8H_{14}O$. Calculated: MR_α 38.38.

0.1728 g substance: 0.4826 g CO_2; 0.1750 g H_2O.
0.2555 g substance: 0.7113 g CO_2; 0.2577 g H_2O.
Found %: C 76.06, 75.93; H 11.33, 11.28.
$C_8H_{14}O$. Calculated %: C 76.19; H 11.11.

Molecular weight determination (cryoscopic)

0.2640 g substance: 12.2 g benzene: Δt 0.87°
Found: M 127.
$C_8H_{14}O$. Calculated: M 126.

We synthesized the semicarbazone of our ketone. Its m.p. after initial recrystallization from alcohol was 163°. Its m.p. after another recrystallization, from benzene, was 163-164°.

0.0849 g substance: 17.4 ml N_2 (22°, 740 mm).
0.0732 g substance: 15.2 ml N_2 (22°, 740 mm).
Found %: N 23.19, 23.38.
$C_9H_{17}ON_3$. Calculated %: N 22.94.

The ketone is a mobile, colorless liquid. No polymerization was observed after it had stood for 6 months in a sealed ampoule.

Synthesis of β-Tert-butylvinylacetylenecarboxylic Acid

a) 2 g of metallic sodium was heated to 100° under absolute toluene in a a flask fitted with a ground-in reflux condenser. After the sodium had fused, the flask was closed by a stopper, wrapped in a towel, and vigorously shaken. The toluene was then separated by decantation from the finely divided sodium thus produced, and ether was added to cover the sodium.

2 g of the finely divided sodium in ether was placed in a flask fitted with a stirrer, a mercury seal, and a dropping funnel. The hydrocarbon, β-tert-butylvinylacetylene, diluted with ether, was added drop by drop to the reaction mixture. At the beginning of the reaction, slight evolution of heat was observed, after which the flask was heated to the boiling point of ether for 4 hours. A small amount of the sodium derivative precipitated out, most of the sodium not entering into the reaction.

b) In an effort to increase the yield of the sodium derivative we tried to synthesize the sodium derivative in toluene-ether medium.

9 g of the hydrocarbon, diluted with 2 volumes of ether, was added to 2 g of finely divided sodium in toluene. The mixture warmed up to 30-40° when the hydrocarbon was added. After all the hydrocarbon had been added, the reaction mass was heated for another 3 hours. A precipitate of the sodium derivative settled out. Metallic sodium was left on the bottom of the flask. The next day dry carbon-dioxide gas was passed through the reaction mass for 14 hours. The precipitate of sodium salt was decanted together with the solvent and the sodium and dissolved in water. The precipitate with its traces of sodium was decomposed by methanol.

The aqueous layer was extracted with ether to eliminate the unreacted

hydrocarbon, after which it was acidulated with dilute sulfuric acid. An oily layer floated to the top, and it was extracted with ether. The ether was evaporated in a stream of CO_2. After decomposition with methanol, the precipitate with the sodium was treated in exactly the same manner.

This yielded 2 g of acid, or 16% of theory. B.p. 122° at 6 mm. The acid is a viscous, highly unstable, glycerinelike liquid. It grows dark and polymerizes very quickly when left to stand, even in sealed ampoules.

c) Extremely reactive sodium (sodium dust) was prepared by vigorously shaking sodium that was fused under boiling xylene. The grain size may vary widely, depending upon the amount of shaking, and may even consist of particles that cannot be seen with the naked eye.

10 g of the hydrocarbon was added to 2 g of the sodium dust in xylene. The hydrocarbon reacted vigorously with the sodium. The temperature of the reaction mass rose to 70-80°. The whole flask was filled with a precipitate of the sodium derivative. Dry carbon-dioxide gas was then passed through the reaction mixture for 30 hours. The sodium salt of the acid was extracted with 3 batches of water. The aqueous layer was separated from the xylene and acidulated with dilute sulfuric acid, and the β-tert-butylvinylacetylenecarboxylic acid was extracted with ether.

The ether extract was almost colorless, all the tarry impurities remaining in the xylene. The ether was exhausted in a stream of CO_2. B.p. of the acid = 121° at 6 mm. Yield of crude product was about 40% of theory.

Determination of the Acid Equivalent

0.3025 g substance: required 19.45 ml 0.1N NaOH.
0.3651 g substance: required 23.6 ml 0.1N NaOH.
Found: Equiv. 155, 154.6.
$C_9H_{12}O_2$. Calculated: Equiv. 152.

After the acid had been titrated, a solution of silver nitrate was added to the flask. The silver nitrate was added in excess, about 2.5 times as much as required by theory. An abundant amount of white precipitate, the silver salt, settled out. The silver salt was filtered out and washed with a small amount of distilled water.

0.0946 g substance: 0.0474 g Ag.
0.1292 g substance: 0.0643 g Ag.
Found %: Ag 50.10, 49.76.
$C_9H_{11}O_2Ag \cdot AgNO_3$. Calculated %: Ag 50.03.

The silver salt was synthesized in the same manner once again. Its analysis yielded the same result.

But when high dilutions are employed, the composition of the salt changes. A third sample was precipitated, from a highly diluted acid (0.3 g of acid in 200 ml of water); the precipitate was carefully washed with water.

0.0860 g substance: 0.409 g Ag.
0.0467 g substance: 0.222 g Ag.
Found %: Ag 47.55, 47.53.
$C_9H_{11}O_2Ag$. Calculated %: Ag 41.69.
$C_9H_{11}O_2Ag \cdot AgNO_3$. Calculated %: Ag 50.03.

The silver salt was decomposed by hydrochloric acid. The β-tert-butylvinylacetylenecarboxylic acid was extracted with ether, and the ether was exhausted. Oily drops with the acrid smell of the acid remained in the flask.

Synthesis of the Ethyl Ester of β-Tert-butylvinylacetylene-carboxylic Acid

10 g of the hydrocarbon was added to 2 g of finely divided sodium in xylene. A vigorous reaction between the sodium and the hydrocarbon sets in at once. All the sodium is converted into the sodium derivative, without a residue. The xylene was decanted from the precipitate, and the sodium derivative was washed with ether. The xylene and the ether with which the sodium derivative had been washed were saturated with carbon-dioxide gas and used to recover the acid, since metal derivatives often dissolve in xylene.

6 g of ethyl chlorocarbonate was added to the sodium acetylide in an ether solution. The reaction mass was stirred for 3 hours, after which the sodium chloride was filtered out, the ether exhausted, and the residue distilled in vacuum.

B.p. 87-89° at 6 mm; d_4^{18} 0.9460; n_α^{18} 1.45766; MR_α 51.91.

$C_{11}H_{16}O_2$. Calculated: MR_α 5193.

0.1946 g substance: 0.5180 g CO_2; 0.1489 g H_2O.

Found %: C 72.61; H 8.56.

$C_{11}H_{16}O_2$. Calculated %: C 73.33; H 8.88.

The ethyl ester of β-tert-butylvinylacetylenecarboxylic acid is a mobile liquid with a pleasant apple odor.

SUMMARY

1. The unsaturated ketone 4,4'-dimethyl-3-methenepentanone-2 was synthesized by the hydration of β-tert-butylvinylacetylene.

2. The method of synthesizing β-tert-butylvinylacetylenecarboxylic acid is described.

3. The ethyl ester of β-tert-butylvinylacetylenecarboxylic acid has been synthesized.

LITERATURE CITED

[1] Helmut Schreiber, Ber., 55, 2912 (1922).

[2] Grignard, Bl. Soc. chim., (3) 21, 576 (1899).

[3] I.A.Favorskaya, J. Gen. Chem. USSR, 18, 52 (1948).

[4] Churbakov, J. Appl. Chem. USSR, 13, 1464 (1940).

[5] K.A.Ogloblin, J. Gen. Chem., 18, 2153 (1948).

[6] Carothers and Berchet, J. Am. Chem. Soc., 55, 1094 (1933).

[7] I.N.Nazarov and M.V.Kuvarzina, Izvest. Akad. Nauk, USSR, Div. Chem. Sci., No. 3, 677 (1938).

[8] Charles Moureu, German patent 158252, 1905.

[9] Charles Moureu, Bl. Soc. chim., (3) 25, 303 (1901).

[10] S. Nametkin and V. Isagulyants, Oils and Fats, Nos. 1 - 4, (1935).

Received January 7, 1948

REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

III. 1-BUTOXYCYCLOPROPANE-2-CARBOXYLIC ACID

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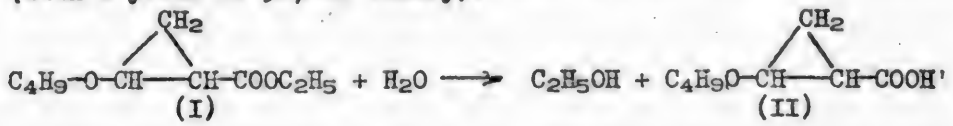
awarded the Order of Lenin

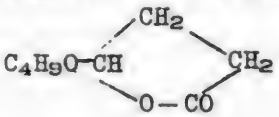
Saponification of the ethyl ester of 1-butoxycyclopropane-2-carboxylic acid (I) [1] in the presence of alkali agents yielded the corresponding acid (II) (with a yield of 90% of theory):



(I) (II)

The properties of thisacid and some if its transformations were investigated. Notwithstanding the fact that the equation for the synthesis of this acid is extremely simple, considerable difficulty is encountered in isolating it from the salt solution, owing to the exceptional propensity of butoxycyclopropanecarboxylic acid to hydrolyze in an acid medium. That is why several different methods of synthesizing the pure preparation were checked experimentally. Products of its hydrolysis: butyl alcohol and an acid with the formula $C_8H_{10}O_5$, were also isolated.

Besides its hydrolyzability, the other most striking property of this acid is the fact that even the purest preparations of this acid apparently contain an admixture of an isomeric lactone (III).



(III)

insofar as we can judge of this by titration.

The lactone was not isolated, which makes the structure ascribed to it even more hypothetical. But in explaining some of the properties and transformations of butoxycyclopropanecarboxylic acid, a possible hypothesis is the preliminary isomerization of the acid to the labile butoxybutyrolactone, which is a derivative of the lactone form of succinaldehydic acid (IV). Thus, it was shown that butoxycyclopropanecarboxylic acid is slowly oxidized by a solution of potassium permanganate, forming succinic and butyric acids.

The specific peculiarity of a cyclic acid, its undergoing hydrolysis with rupture of the three-membered ring, may be referred to its isomeric conversion into the lactone (III), which breaks down readily in acid aqueous solutions,

cleaving off butyl alcohol.

The saponification of the ethyl ester of butoxycyclopropanecarboxylic acid is effected by heating with aqueous or alcoholic solutions of caustic alkalies.

If the saponification is effected in the presence of $Ba(OH)_2$, and the reaction mixture is concentrated after the excess of barium hydroxide has been removed, crystals of the barium salt of the acid $-(C_7H_{13}COO)_2Ba$ – are readily obtained when the solution is cooled.

When solutions of alkaline salts of the acid are acidulated, water-insoluble butoxycyclopropanecarboxylic acid separates out; in most cases this acid suffers partial hydrolysis during this operation, forming butyl alcohol.

It was easy to judge the onset of hydrolysis in these instances by means of the change in the boiling point of the butoxycyclopropanecarboxylic acid: the boiling point drops and becomes unsharp, not characteristic of an individual compound.

Repeated distillation of the viscous and high-boiling acid is difficult and usually does not result in complete separation of the mixture. The acid fraction with the highest boiling point, which distils within a range of 2-3°, has a constant boiling point and has the composition of butoxycyclopropanecarboxylic acid. The fractions that distill at lower temperatures are obviously mixtures with no fixed boiling point, and it is hard to separate them by distillation. This is why we were unable to raise the yield of the pure preparation of the acid beyond 70% of theory, by fractionation, (Table 2), notwithstanding the fact that the yield of the crude product was 90% of theory.

Hydrolysis may be prevented if the isolation of the acid from solutions of its salts is done with maximum care. The ready preparation distills within a narrow temperature range and contains no impurities (yield 90% of theory). The crude preparation, which distils over a wide temperature range, can be purified by means of "reprecipitation" from alkali solutions, provided suitable precautions are observed during acidulation. Most of the impurities remain in the aqueous solution (cf the experimental section of this paper), and the butoxycyclopropanecarboxylic acid can be secured in the pure state.

This operation results in a noticeable diminution of the yield (Table 2), but pure butoxycyclopropanecarboxylic acid can be prepared even from the lowest-boiling fractions of the crude preparation by this method (Experiment 2b). Both of these methods - reprecipitation and distillation - were employed to secure pure preparations of the acid whenever hydrolysis set in as the result of our isolating it from solutions.

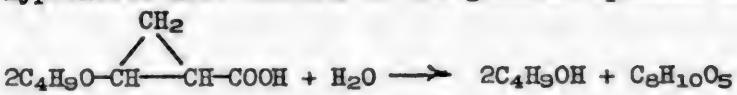
The hydrolysis products were found principally in our examination of the aqueous solutions from which the acid was isolated, viz: butyl alcohol and an aldehydic acid with the formula $C_8H_{10}O_5$, the structure and the mechanism of formation of which are now being studied. We proposed to explain the extraordinary tendency of our acid to hydrolyze, splitting off butyl alcohol, with the aid of a hypothesis that the acid (II) is transformed into the isomeric lactone (III), which in turn decomposes into butyl alcohol and succinaldehydic acid

$$\text{(II)} \longrightarrow \text{(III)} \longrightarrow C_4H_9OH + O = CH - CH_2 - \underset{\displaystyle COOH}{CH_2}$$

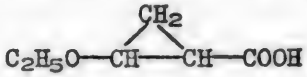
Since we did not isolate succinaldehydic acid, obtaining instead the acid $C_8H_{10}O_5$, we were inclined to believe that the latter was the product of the further transformation of the succinaldehydic acid that is initially formed during

hydrolysis. Not having enough data at the present time to confirm this conjecture, we must also keep in mind an alternative hydrolysis process, in which the intermediate conversion product is 1-hydroxycyclopropane-2-carboxylic acid [1].

Both hypotheses must conform to the general equation of the hydrolysis reaction:



We have not found much detailed information in the literature on 1-alkoxycyclopropane-2-carboxylic acids. Apparently, the only one thus far synthesized is 1-ethoxycyclopropane-2-carboxylic acid, obtained by Rambaud in 1938 [2]:



with an extremely low yield and by a method that is totally different from our own.

In his paper Rambaud does not comment on a tendency of ethoxycyclopropanecarboxylic acid to cleave hydrolytically in an acid medium. Another property is characteristic of it, according to Rambaud: its tendency to oxidize -- even under the influence of atmospheric oxygen -- to succinic acid. Various oxidants act even more quickly (solution of permanganate, chromium trioxide, etc.).

We noticed no changes of any kind when our acid was stored. Potassium permanganate gradually oxidizes butoxycyclopropanecarboxylic acid to succinic and butyric acids, however, even in the cold.

Thus there is a definite, as yet, inexplicable, difference in the properties of the two acids. If the opportunity offers, we propose to synthesize 1-ethoxycyclopropane-2-carboxylic acid.

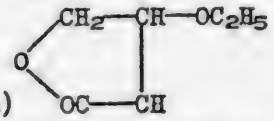
In titration, on the other hand, both acids seem to behave similarly.

In determining the neutralization equivalent of butoxycyclopropanecarboxylic acid by direct titration with 0.1N NaOH, the results are too high, as Rambaud also found. But if a weighed batch of the acid is dissolved in an excess of the 0.1N base and then the excess of the base is titrated back, with heating, against 0.1N sulfuric acid, the results obtained are close to those expected. Using the method of back titration, Rambaud obtained results close to the computed values for the neutralization equivalent of ethoxycyclopropanecarboxylic acid as well. When the warmed solution is directly titrated with 0.1N NaOH, the results obtained differ but little from those computed. This was also true of the ethoxycyclopropanecarboxylic acid.

The sole difference between the butoxy derivative and its ethoxy analogue is that the former's experimentally determined neutralization equivalent does not change after prolonged storage, whereas the latter's value rises from 130 to 500 (according to Rambaud's figures). It should also be noted that the preparations we synthesized in various saponification runs did not always yield identical values for the neutralization equivalent when the determination was made by titration with 0.1N NaOH, in the cold. By employing back titration in these cases we obtained results that agree with one another and with the calculated value of the neutralization equivalent.

Rambaud advanced the hypothesis of the existence of an isomeric lactone, present as an impurity of the ethoxycyclopropanecarboxylic acid in the preparations

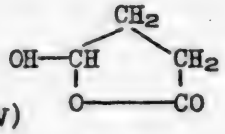
of that acid synthesized by him, as an explanation of this discrepancy between his experimental findings and the computed neutralization equivalent. This lactone is not affected (or is only slowly affected) by alkalies in the cold, but its ring is opened when heated with an excess of alkali.



(III,a)

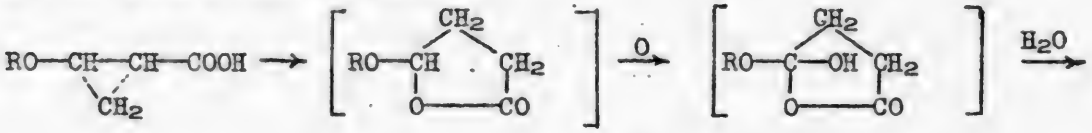
That is why direct titration of a weighed quantity of the acid with 0.1N alkali in the cold does not yield the results called for by theory. Rambaud believes that the rise in the neutralization equivalent of the ethoxy acid from 130 to 500 during storage is due to the gradual conversion of the cyclic acid into its isomeric lactone. According to Rambaud, this transformation is related to the formation of succinic acid when the cyclic acid is oxidized.

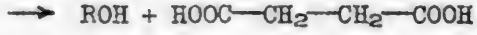
We may assume, in agreement with Rambaud, that the lactone form is produced in the case of our acid as well, inasmuch as we found a discrepancy in the results obtained with direct and back titration. But it seemed to us to be more probable that for both of these alkoxy acids the isomeric lactone has a somewhat different structure than that assigned to it by Rambaud. For we are rather inclined to assign it the formula (III), which is easily derived from the lactone form of succinaldehydic acid (IV) and may be looked upon as the hemiacetal of the latter.



(IV)

In fact, if Rambaud's formula is employed, it is hard to explain the conversion of the alkoxy acid into succinic acid via the lactone (III,a), as the French author conjectured; the lactone (III,a) should not yield succinic acid upon oxidation. Besides, this conversion is easily explainable by means of the formula (III) we propose:





The following comparison may indicate the relationship between isomerization to a lactone and oxidation of the alkoxyacids to succinic acid. Rambaud's ethoxy acid changes its neutralization equivalent when allowed to stand for a long time in a closed container, owing to its conversion into a lactone, but is oxidized to succinic acid when kept exposed to the air. Our acid's neutralization equivalent does not change appreciably during storage and is oxidized to succinic acid only after prolonged agitation with a permanganate solution. At the present time it is hard to decide whether this more difficult oxidizability is due to the slower conversion into a lactone or to the fact that such a conversion does not occur at all and the acid itself undergoes oxidation.*

*It should be borne in mind, however, that the ethyl ester of butoxycyclopropanecarboxylic acid, for which the isomeric lactone form is impossible, is oxidized by a permanganate solytion only after heating (cf. the preceding report).

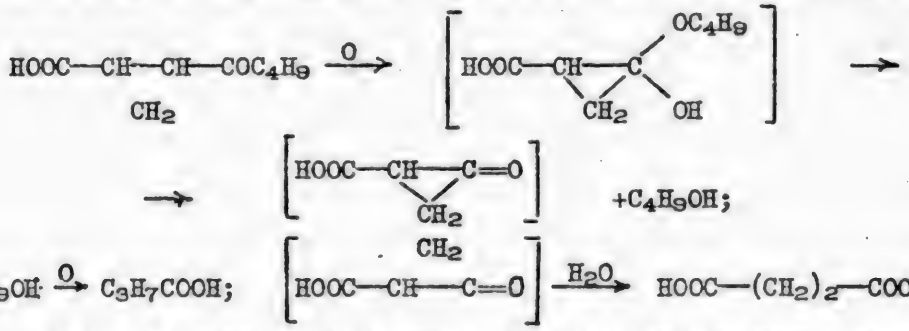
As has just been pointed out, the specific tendency of the acid to cleave hydrolytically may also be related to its isomeric conversion to a lactone, which may occur under the influence of hydrogen ions.

About 10 days were needed for complete oxidation of 39 g of the acid by potassium permanganate in the cold. Thus, butoxycyclopropanecarboxylic acid is oxidized much more slowly than compounds with multiple bonds. Moreover, the assumption that the acid we have investigated might have the structure of an unsaturated acid with an open chain of atoms:

$C_4H_9O{-}CH{=}CH{-}CH_2{-}COOH$ or $C_4H_9O{-}CH_2{-}CH{=}CH{-}COOH$

falls of its own weight, since neither of these formulas would yield succinic acid when oxidized by permanganate.

As for the mechanism of the acid's oxidation, the intermediate genesis of the easily changeable lactone is fully admissible in this reaction for a number of considerations. It is not impossible, however, that the oxidizing agent attacks the three-carbon-atom ring of the acid itself, where the already oxidized atom of the ring will be the most vulnerable spot for the oxidant:



Both of these probable mechanisms involve the same consumption of the oxidizing agent, viz.: 3 gram equivalents of oxygen per mole of acid. Experiment showed that the consumption of the oxidizing agent exceeds the amount computed according to these equations (4 gram equivalents of oxygen per mole of acid), apparently due to some oxidation side reactions that are not covered by either equation.

EXPERIMENTAL

1. Synthesis of 1-Butoxycyclopropanecarboxylic Acid

Saponification of the ester of butoxycyclopropanecarboxylic acid (I) was effected in the following ways:

a) Heating with an alcoholic solution of potassium hydroxide;

b) Heating with aqueous solutions of caustic alkalies;

c) Heating with a solution of barium hydroxide.

a) 19 g of the ester (I) was mixed with 120 ml of a 15% alcoholic solution of potassium hydroxide, and the reaction mixture was heated for a short time over a water bath until the alcohol boiled. The solution was then cooled to room temperature, diluted with water to a total volume of 600 ml, and acidulated with dilute sulfuric acid while chilled by ice. The oily butoxycyclopropanecarboxylic acid that separated out at the top of the solution was separated from the aqueous layer, which was then shaken up repeatedly with ether. The ether extracts, combined with the principal reaction product, were desiccated

over anhydrous sodium sulfate. The ether was driven off over a water bath, and the acid that remained wasdriven off in vacuum. B.p. 143-144° at 12 mm. The yield of the acid was 14.2 g (92% of the theoretical yield).

b) 56 g of the ester (I) was mixed with 400 ml of a 5% aqueous solution of potassium hydroxide, and the reaction mixture was heated over an open flame, with rapid stirring, until the reaction mixture had become completely homogeneous. When this had been attained, a current of carbon-dioxide gas was passed through the reaction mixture, which had been cooled to room temperature, to neutralize the excess potassium hydroxide. The solution was then concentrated in vacuum to a volume of about 100 ml and placed in a 1-liter separating funnel after it had cooled. A layer of ether was added to cover the solution, and 5% sulfuric acid was introduced under the ether layer by means of a pipette, about 10 ml at a time. The emulsion of the cyclic acid that formed when the solution was acidulated was immediately transferred to the ether layer by shaking the separating funnel. The sulfuric acid was added until no more cloudiness was observed in the aqueous solution; then the ether extracts were desiccated over anhydrous sodium sulfate, and the ether was driven off. The residue, distilled in vacuum, was the almost pure acid:

Fraction 1: b.p. 134-135° at 8 mm – 2 g.
Fraction 2: b.p. 135-137° at 8 mm – 42.5 g.

The acid yield, taking both fractions together, was 44.5 g (94% of the theoretical yield).

Note: After the addition of the sulfuric acid to the aqueous solution of the salt had been completed, we usually shook the solution up once more with a fresh batch of ether. Careful extraction of the aqueous solution with ether after acidulation results, however, in contaminating the acid with products of its hydrolytic decomposition that enter the ether from the aqueous layer. The ether may be replaced by benzene in separating the butoxycyclopropanecarboxylic acid from the solution of its salt.

c) 18.6 g of the ester (I) (0.1 mole) was mixed with 200 ml of water and 32 g of barium hydroxide [$Ba(OH)_2 \cdot 8H_2O$]. During mixing the reaction mixture was boiled until the solution cleared. After it had cooled, the solution was saturated with carbon-dioxide gas to eliminate the barium hydroxide, which had been used in excess, from the solution. The barium carbonate was filtered out with suction, and the filtrate was concentrated over a water bath. Upon cooling, the solution, concentrated down to small volume, deposited the barium salt of butoxycyclopropanecarboxylic acid, which crystallized as large white needles. Evaporation of the filtrate to dryness yielded 20.7 g of the barium salt (91% of theory); its analysis is given below. We did not isolate the free acid from its barium salt.

Table 1 gives the comparative results of our efforts to synthesize butoxycyclopropanecarboxylic acid by these various methods.

2. Separation of Butoxycyclopropanecarboxylic Acid From Solutions

If certain precautions were not observed when solutions of salts of the cyclic acid were acidulated, partial hydrolysis took place, and the isolated product did not have a sharp boiling point. To secure a pure preparation the crude reaction product was either reprecipitated from alkali solutions (2 a) or fractionated in vacuum (2 b). We were able to separate the hydrolysis products only by purifying the crude preparation. The results of these experiments are listed in Table 2; they are described below under 2 a and 2 b.

TABLE 1

Experiments to Secure a Pure Preparation of Butoxycyclopropane carboxylic Acid

Test No.	Grams of the trimethylene ester (I)	Saponifying agent	Boiling point of butoxycyclopropanecarboxylic acid	Acid yield, in % of theory
1	9.3	60 ml of a 15% alcoholic solution of potassium hydroxide	147-150° at 16 mm	75
2	19.0	120 ml of a 15% alcoholic solution of potassium hydroxide	143-144° at 12 mm	92
3	33.5	175 ml of a 10% aqueous solution of potassium hydroxide	136-139° at 9 mm	90
4	56	400 ml of a 5% aqueous solution of potassium hydroxide	134-137° at 8 mm	94
5	22	100 ml of a 5% aqueous solution of potassium hydroxide	126.5-128° at 4 mm	91

TABLE 2

Experiments to Secure and to Purify the "Crude" Preparation of Butoxycyclopropanecarboxylic Acid

Test No	Grams of the trimethylene ester	Saponifying agent	B.p. of the "crude" acid	Yield* of crude reaction product, %	Method of purifying the crude preparation	B.p. of the pure acid	Yield of the pure preparation, %
1	46.5	Solution of 20% KOH in 150 ml of alcohol	114-123° at 0.5mm	88	Reprecipitation	136-137.5° at 9 mm	57
2	112	500 ml 10% aqueous solution of KOH	125-135° at 8 mm	95	Reprecipitation	134-136° at 8 mm	43
3	112	800 ml 5% aq. solu. KOH	124-139° at 10 mm	87.1	Reprecip., followed by fract.	134-136° at 8 mm	53
4	65	300 ml 5% aq. solu. KOH	128-138° at 8 mm	93.2	Fractionation	134.5-138° at 8 mm	73

*Yield based on the initial trimethylene ester.

a) Reprecipitation test of butoxycyclopropanecarboxylic acid. Separation of the Products of Hydrolysis. To secure a pure preparation of the acid by means of "reprecipitation", the crude product synthesized in Experiment 2 (Table 2) and containing hydrolysis products as impurities was used (b.p. 125-135° at 8 mm).

84.5 g of this preparation was neutralized with a 10% solution of KOH, and the neutral solution was shaken up with ether. After desiccation and driving off the solvent, the residue was distilled at ordinary pressure. The distillate weighed 5 g and consisted of nearly pure butyl alcohol: d_4^{20} 0.813; n_α^{20} 1.397; b.p. 116-117°.

The rest of the butyl alcohol was eliminated from the solution by driving off part of the solution. To the solution thus concentrated, dilute sulfuric acid was carefully added, with thorough stirring and external chilling, in an excess that did not greatly exceed the computed quantity.

The butoxycyclopropanecarboxylic acid that separated out as an oily layer after acidulation was extracted with ether and distilled in vacuum after the solvent had been removed. B.p. 134-136° at 8 mm. Yield: 41 g (43% of theory).

Another product of hydrolysis was found upon examination of the aqueous layer left after isolation of the butoxycyclopropanecarboxylic acid. This was done by neutralizing the aqueous solution with an alkali, concentrating it over a water bath and then in vacuum to a volume of 170 ml, and again acidulating it with 30% sulfuric acid. The mineral salts that separated out as a result of this treatment were filtered out, the filtrate being placed in an extractor.

About 2 g of a yellow liquid that is insoluble in ether and a somewhat larger quantity of a crystalline substance were recovered from the ether extracts after two days of extraction with ether. The crystals were recrystallized from alcohol, in which they were highly soluble, even in the cold. They proved to be nearly insoluble in other solvents, including water. They dissolved with difficulty in ether.

Their melting point (99-100°) remained constant after double recrystallization. The yield was 5.7 g.

0.1530 g substance: 0.2899 g CO_2; 0.0779 g H_2O.
0.1508 g substance: 0.2844 g CO_2; 0.0764 g H_2O.
Found %: C 51.68, 51.44; H 5.70, 5.67.
$C_8H_{10}O_5$. Calculated %: C 51.61; H 5.42.

It was established by preliminary research that this compound is an aldehydic acid. Its structure and the mechanism of its formation are now being investigated.

The oily liquid is converted into a thick tar by heating in vacuum (8 mm). Ether extraction of this tarry mass yielded a small quantity of crystals that fused at about 100° and were apparently of the same composition as the $C_8H_{10}O_5$ acid we had synthesized.

b) Fractionation, followed by reprecipitation. 35 g of the acid preparation, with a b.p. of 114-123° at 0.5 mm, was fractionated in a column with a wide dephlegmator. The acid is a viscous liquid, which makes its distillation difficult. Several distillation runs yielded:

Fraction 1: b.p. 118-127° at 8 mm – 5 g
Fraction 2: b.p. 127-134° at 8 mm – 8.6 g
Fraction 3: b.p. 134-136° at 8 mm – 19 g

Fractions 1 and 2, totalling 13.6 g, were combined and dissolved in the

requisite quantity of alkali. Recovery of the acid from the solution of its sodium salt was effected by the method described in the synthesis of the acid (1 b). Distillation yielded 6.5 g of acid with a b.p. of 134-136° at 8 mm.

Thus, including Fraction 3, we got 25.5 g of acid with a b.p. of 134-136° at 8 mm, or 73% of theory.

Physical Constants and Molecular Refraction of Butoxycyclopropanecarboxylic Acid

B.p. 143-144.5° at 12 mm; d_4^0 1.035; d_4^{14} 1.024; d_4^{20} 1.020. n_α^{14} 1.444; n_α^{20} 1.442. Found: MR_α 41.02, 41.00.
$C_8H_{14}O_3$. Calculated: MR_α 39.94.
Increment: 1.08, 1.06.*

Analysis of the acid and its salts:

0.1287 g substance: 0.2879 g CO_2: 0.1074 g H_2O.
0.1594 g substance: 0.3568 g CO_2; 0.1302 g H_2O.
Found %: C 61.05, 61.04; H 9.34, 9.14.
$C_8H_{14}O_3$. Calculated %: C 60.72; H 8.92.
0.2155 g substance: 20.21 g of acetic acid: Δt 0.26.
0.3535 g substance; 20.21 g of acetic acid: Δt 0.44.
Found: M 159.9, 155.0.
$C_8H_{14}O_3$. Calculated: M 158.1.

The silver salt of the acid is only slightly soluble in water. It decomposes quite violently upon heating, which hampers the determination of the silver content:

0.1286 g substance: 0.0698 g AgCl.
Found %: Ag 40.93.
$C_8H_{13}O_3Ag$. Calculated %: Ag 40.74.

The foregoing analysis was made of the silver salt of the acid with a b.p. of 143-144.5° at 8 mm. To check the purity of the preparation that distills in the 134.5-138° range at 8 mm, two fractions of silver salts, obtained by fractional precipitation of the ammonium salt of this preparation with a solution of lunar caustic, were analyzed:

Fraction 1: 0.1704 g substance: 0.0696 g Ag.
0.1404 g substance: 0.0568 g Ag.
Found %: Ag 40.83, 40.46.
$C_8H_{13}O_3Ag$. Calculated %: Ag 40.74.

Fraction 2: 0.1456 g salt: 0.0587 g Ag.
Found %: Ag 40.24.
$C_8H_{13}O_3Ag$. Calculated %: Ag 40.74.

Thus, both fractions proved, upon analysis, to be close enough to the expected results.

Analysis of the barium salt obtained in Experiment (1 c) yielded the following results:

0.2087 g substance: 0.1064 g $BaSO_4$.
0.1963 g substance: 0.1019 g $BaSO_4$.
Found %: Ba 30.00, 30.46.
$C_{16}H_{26}O_6Ba$. Calculated %: Ba 30.41.

* Rambaud [2] found an increment of 1.00 for 1-ethoxycyclopropane-2-carboxylic acid.

Neutralization equivalent. The following were the results of titrating an accurately weighed quantity of the acid with a b.p. of 135-137° at 8 mm by 0.1N NaOH.

0.1502 g substance: 9.5 ml 0.1N NaOH (φ = 0.865).
0.1640 g substance: 10.4 ml 0.1N NaOH (φ= 0.865).
Found: equiv. 182.8, 182.3.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

Direct titration, without heating:
0.3000 g substance: 21.5 ml 0.1N NaOH (φ = 0.9755).
0.2413 g substance: 17.25 ml 0.1N NaOH (φ = 0.9755).
Found: equiv. 161.1, 161.7.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

Direct titration of the heated solution:
0.2144 g substance: 13.4 ml NaOH (φ = 0.9755)
Found: equiv. 161.4.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

Back titration with 0.1N H_2SO_4. The weighed quantity of acid was first dissolved, with heating, in an excess of 0.1N NaOH.

0.3000 g substance: 32.2 ml 0.1N NaOH (φ= 0.865); 10.9 ml 0.1N H_2SO_4 (φ= 0.812).
0.2413 g substance: 28.0 ml 0.1N NaOH (φ= 0.865); 11.1 ml 0.1N H_2SO_4 (φ= 0.812).
Found: equiv.157.9, 157.7.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

These determinations were made with a preparation of the acid synthesized in a different saponification experiment: b.p. 134-136° at 8 mm. The determination was made several months after its synthesis:

Direct titration without heating (0.1N NaOH):
Found: equiv.166.0.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

Direct titration of the heated solution:
Found: equiv. 162.0, 162.0.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

Back titration with 0.1N H_2SO_4. The weighed quantity of the acid was first dissolved, with heating, in an excess of 0.1N NaOH:
Found: equiv. 159.0
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

If the foregoing determinations are made immediately after the butoxycyclopropanecarboxylic acid is synthesized, the titration results remain unchanged:

Direct titration without heating:
Found: equiv. 167, 167.1.
$(C_7H_{13}O)CO_2H$. Calculated: equiv. 158.1.

The discrepancy between the experimental and the computed values of the neutralization equivalent when direct titration with tenth-normal alkali in the cold was employed was attributed to the presence of the isomeric lactone (III) in the acid.

3. Oxidation of 1-butoxy-2-cyclopropanecarboxylic Acid.

39 g of the acid with a b.p. of 134-136° at 8 mm was shaken up in the cold with 70 ml of a 2% solution of permanganate. As soon as the solution was

decolorized, new batches of permanganate in dry, finely powdered form were added. A total of 108 g of potassium permanganate was required for complete oxidation, the entire process of oxidation taking about 10 days (butoxycyclopropanecarboxylic acid is oxidized much more slowly by permanganate than are unsaturated compounds). After the manganese dioxide had been filtered out, the solution was distilled. When the distillate was decanted from a solution of p-nitrophenylhydrazine acetate, we got a small quantity of a tarry deposit of the p-nitrophenylhydrazone, which we were unable to characterize.

The oxidation solution was concentrated (in vacuum) and then acidulated with sulfuric acid. The small oily layer of acid that separated out when the solution was acidulated was extracted with ether. The liquid acid remaining after the ether had been driven off was distilled (cf the investigation of liquid acids), and the aqueous solution separated from the ether extracts was again extracted with ether, but this time in a continuous percolator. This last extraction yielded about 6 g of solid acid as large, colorless lamellae.

a) Investigation of the solid acid. The solid acid fused at 183-184° after recrystallization from hot water and was succinic acid, according to the analytical data.

Neutralization equivalent:

0.1519 g substance: 27.1 ml NaOH 0.1N ($\varphi = 0.9755$)
0.1449 g substance: 25.6 ml NaOH 0.1N ($\varphi = 0.9755$)
Found: equiv. 58.65, 58.03.
$C_2H_4(COOH)_2$. Calculated: equiv. 59.00.

Analysis of the silver salt:

0.1604 g substance: 0.1035 g Ag.
Found %: Ag 64.52.
$C_4H_4O_4Ag_2$. Calculated %: Ag 64.60.

A test sample exhibited no depression when mixed with standard succinic acid.

b) Investigation of the liquid acids. The following fractions were obtained when the liquid acids were distilled:

Fraction 1: b.p. 110-125° at 760 mm, weight 0.6 g.
Fraction 2: b.p. 51-58° at 7 mm, weight 5.6 g.
Fraction 3: b.p. 58-130° at 7 mm, weight 0.5 g.

The residue was a mixture of liquid acids and succinic acid.

The residue was steam distilled to separate the liquid acids from the succinic acid. The distillate was extracted with ether. The ether extracts were desiccated, and the ether then driven off over a water bath. The residue was distilled at ordinary pressure; 1st fraction: b.p. 100-155°; 2nd fraction: b.p. 155-170°.

The first fraction was not explored owing to its wide range of boiling points, but the second fraction was combined with the second fraction of the initial distillation of the liquid acids.

The combined fractions were redistilled; this yielded: 2 g of an acid with a b.p. of 151-156°; and 4 g of an acid with a b.p. of 156-158°.

The distillate with a b.p. of 156-158° was investigated, and the data obtained were compared with the computed data (or the data known from the literature) for butyric acid:

	B.p.	d_4^0	$d_4^{18.5}$	d_4^{20}	n_α^{17}	n_α^{20}
Acid investigated	156-158°	0.983	0.965	0.963	1.3954	–
Butyric acid	162°	0.975	–	0.960	–	1.3955

Found: MR_α 21.85
$C_4H_8O_2$. Calculated: MR_α 22.21.

Neutralization equivalent:

0.3461 g substance: 42.7 ml 0.1N NaOH (φ = 0.9755).
0.2669 g substance: 32.8 ml 0.1N NaOH (φ = 0.9755).
Found: equiv. 83.10, 83.43.
C_3H_7COOH. Calculated: equiv. 88.06.

The lack of complete agreement between the computed and experimental results was attributed to the effect of traces of other acids synthesized as the result of oxidation side reactions not provided for in the equation given on page a531.

Analysis of the individual fractions of the silver salts, prepared from this acid by fractional precipitation, left no doubt, however, that the acid under investigation actually is butyric acid (the 2nd and 3rd fractions of the salts):

Fraction 1

0.1854 g substance: 0.1063 g Ag.
0.1565 g substance: 0.0896 g Ag.
Found %: Ag 57.32, 57.23.

Fraction 2

0.1720 g substance: 0.0954 g Ag.
0.0645 g substance: 0.0358 g Ag.
Found %: Ag 55.46, 55.50.

Fraction 3

0.1164 g substance: 0.0644 g Ag
Found %: Ag 55.33
$C_3H_7CO_2Ag$. Calculated %: Ag 55.35.

SUMMARY

1. 1-Butoxycyclopropanecarboxylic acid can be synthesized from its ethyl ester with a yield of as much as 90% of theory by the action of aqueous or alcoholic solutions of caustic alkalies.

2. Butoxycyclopropanecarboxylic acid possesses the unusual property of being hydrolyzed by dilute acids, yielding butyl alcohol and an acid with the composition $C_8H_{10}O_5$. This ready hydrolyzability makes the securing of a pure preparation of the acid with a constant boiling point quite difficult.

3. The titration data force us to assume that the acid contains an impurity in the shape of the isomeric butoxybutyrolactone. The latter may be an intermediate form through which conversion takes place in the processes of hydrolysis and oxidation of the cyclic acid.

4. Butoxycyclopropanecarboxylic acid is slowly oxidized by a permanganate solution to succinic and butyric acids, which testifies to its cyclic structure.

LITERATURE CITED

[1] I. Dyakonov (Report 1), J. Gen. Chem., 19, 1891 (1949).

[2] Rambaud, Bull. Soc. Chim. (5), 5, 1560 (1938).

Received June 24, 1948.

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* See CB translation p. a355 ff.

RESEARCH IN THE FIELD OF THE α-KETONIC ETHERS

III. THE SELECTIVITY OF HYDROGENATION OF BENZALACETONE ETHER IN THE PRESENCE OF PLATINUM AND PALLADIUM

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Leningrad State University, awarded the Order of Lenin

In our first paper on the hydrogenation of α-ketonic ethers [1] we showed that when hydrogen is added to benzalacetone ether in the presence of platinum black, the process takes place selectively, hydrogen being added to the carbonyl group. The principal product formed is the ether of an unsaturated alcohol: methylstyrylcarbinol, and reduction to a glycol, $C_6H_5-CH_2-CHOH-CHOH-CH_3$, is often observed.

In our previous report [2], we showed that tert-butylstyryl ketone ether is not hydrogenated over Pt black, but adds hydrogen sharply and selectively when the more active catalyst Pd/Ni is used, the oxide ring being ruptured and an α-ketol being formed.

In this instance we did not find that the ketol was further reduced to a glycol.

What has been just said made it appear interesting to effect the hydrogenation of benzalacetone ether over a Pd/Ni catalyst under the conditions we employed to hydrogenate tert-butylstyryl ketone ether.

Under these conditions, benzalacetone ether (the ether of methylstyryl ketone) adds hydrogen sharply selectively, hydrogenation practically ceasing when 1 mole of hydrogen has been absorbed. The only reaction product is an α-ketol: benzylacetylcarbinol (II).

The conclusion that the process follows another course when Pd/Ni is used as a catalyst instead of Pt black was based on a comparison of the constants of the products obtained in hydrogenation with these catalysts, or on proof of the structures of the substances synthesized in the present paper.

The product of the hydrogenation of benzalacetone ether over Pd/Ni is a slightly yellow liquid with a b.p. of 96° at 1 mm; d_4^{19} 1.0853; n_α^{19} 1.52403.

The product of the hydrogenation of benzalacetone ether over Pt black, which is methylstyrylcarbinol ether, as was proved earlier [1], has the following constants: b.p. 128-130° at 3 mm; $d_4^{10.5}$ 1.105; $n_\alpha^{10.5}$ 1.53233.

Direct comparison of the boiling point of the compound we synthesized with that of methylstyrylcarbinol ether sufficed to indicate the difference between the products obtained when Pt black and Pd/Ni were used as catalysts.

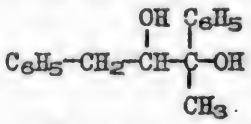
The product of hydrogenation over Pd/Ni yields a semicarbazone with a m.p. of 169-170°, and an oxazone with a m.p. of 171-173°, which indicates the presence of an oxy-ketone group. The conjectured ketol - benzylacetylcarbinol - and its semicarbazone

described in the literature. Muller and Pechmann [3] give the m.p. of benzylmethyl diketone as 172-173°.

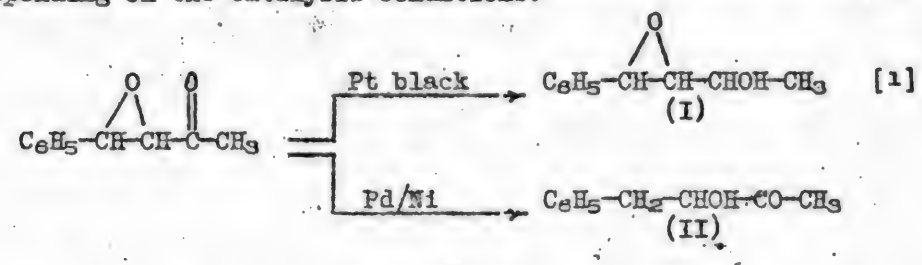
Quantitative determination of the amount of the α-ketol in the end product by means of Fehling's solution indicated that under these conditions hydrogenation follows but one course, rupturing the oxide ring at the phenyl side.

It should be noted that the figures resulting from the quantitative determination – 94.5 and 95.5% of the ketol – are somewhat low (cf the expermental section of this paper), since under these conditions (heating for 30 minutes in an alkaline medium) the α-ketol undergoes a change (apparently a ketol condensation), as was proved by means of a special test.

The structure of the synthesized ketol was proved by converting it into a glycol by the action of C_6H_5MgBr, followed by the oxidation of the glycol with chromic trioxide; treatment of the oxidation products yielded acetophenone, identified as its semicarbazone with a m.p. of 198-199°., which gave no depression when fused with the known semicarbazone of acetophenone. Benzoic acid was isolated from the acid products of oxidation. It follows, therefore, that the structure of the glycol is as follows:



Comparison of the results of this research with those of a previous one [1] showed that hydrogenation of benzalacetone ether either caused only the rupture of the oxide ring or else involved the hydrogenation of the carbonyl group, depending on the catalysis conditions.



[1]

We were interested in ascertaining whether the hydrogenation processes follow the same course no matter what solvent was used or how the catalyst was prepared: does Pt always cause the hydrogenation of the carbonyl group, while Pd ruptures the oxide ring to form an α-ketol. To find out we made a series of tests to hydrogenate benzalacetone ether over Pd and Pt under varying conditions.

It should be noted that the ketol (II) can be easily identified by synthesizing the semicarbazone; it is impossible to demonstrate the presence of methylstyrylcarbinol ether (I) by converting it into a characteristic crystalline derivative when only small amounts are available for research. For this reason, the only way we were able to establish the direction of the reaction: toward the formation of the ether of an unsaturated alcohol (I), in our experiments was by means of a negative reaction with semicarbazide and the higher boiling point of the product after it had absorbed 1 mole of H_2. The addition product with 2 moles of H_2 – methylbenzylethylglycol – which boils at a much higher temperature, was left in the distilling flask.

Boiling point of benzylacetylcarbinol: 96° at 1 mm.

Boiling point of methylstyrylcarbinol ether: 128-130° at 3 mm [1]:
Boiling point of benzalacetone ether: 123-125° at 7 mm [1].
Boiling point of methylbenzylethylcarbinol: 154-155° at 10 mm [1].

In some of the experiments, a semicarbazone with a m.p. (149-154° in Experiment 5) that lay between the m.p. of the semicarbazone of benzalacetone ether (140-141°) and the m.p. of the semicarbazone of benzylacetylcarbinol (169-170°) was formed in a semicarbazide solution after treatment of the substance recovered after hydrogenation. Proving the presence of the α-ketol in the hydrogenation product in this instance required that it be freed of its accompanying oxide. This was done by treating the synthesized fraction with water in the presence of 5% H_2SO_4 to hydrolyze the oxide; hydrolysis yielded a mixture of a dihydroxy ketone and a ketol.

Ether extraction was employed to separate the latter; the ketol readily entered into ether solution, while the dihydroxy ketone remained in the aqueous solution. The semicarbazone, with a m.p. of 168-169°, was synthesized from the substance that remained after the ether had been driven off; a test sample mixed with the known semicarbazone of benzylacetylcarbinol fused at 168-169°.

The most interesting of our experiments on the hydrogenation of benzalacetone ether in the presence of Pt and Pd under different conditions are listed in Tables 1 and 2.

The data of Table 1 show that the use of Pd as the catalyst makes the hydrogenation process selective, opening the oxide ring no matter what method of preparing the catalyst or what solvent (alcohol or ether) is employed. It may, however, be noted that the hydrogen is added more slowly in ether than in alcohol.

The most active catalyst is Pd/Ni, prepared by the Hinsberg method. The most effective solvent is a mixture of ether and alcohol (Experiment 19); under these conditions the process of absorbing hydrogen is rapid, and the catalysis product can be distilled without further treatment.

When a new batch of benzalacetone ether is hydrogenated over Pd obtained from the hydrogenation process (Experiment 15), the process resembles that over palladium black. Hydrogenation does not occur at high speed, and, hence, the process does not break off sharply after 1 mole of hydrogen has been added. The addition of hydrogen practically ceases, however, after 1 mole of H_2 has been absorbed, and the reaction product is the pure α-ketol.

A different state of affairs prevails when platinum is used as the catalyst, (Table 2). The carbonyl group is then subjected to hydrogenation, and the process is less selective. We were able to turn the process toward the partial formation of the ketol when using a Pt catalyst by adding a small amount of hydrochloric acid (Experiment 5).

It is possible that the addition of HCl tended to increase the reactivity of the oxide ring. The ability of HCl to accelerate the hydrogenation process has been commented on more than once [4]. It should be noted, however, that the experiment took a very long time, and it is not impossible that under these conditions the ether is first isomerized to the diketone, which then undergoes hydrogenation.

In none of the other experiments was the α-ketol formed when hydrogenation was effected in alcoholic or ether solutions and Pt black or Pt/Ni was used as the catalyst. The optimum conditions for synthesizing methylstyrylcarbinol ether (I) were those employed in the initial research – Pt black in

absolute ether. In all the other cases we got mixtures; notwithstanding the fact that the experiment broke off after the absorption of a volume of hydrogen that somewhat exceeded 1 mole, some of the benzalacetone ether did not enter into reaction, while the process partly continued until the glycol was formed.

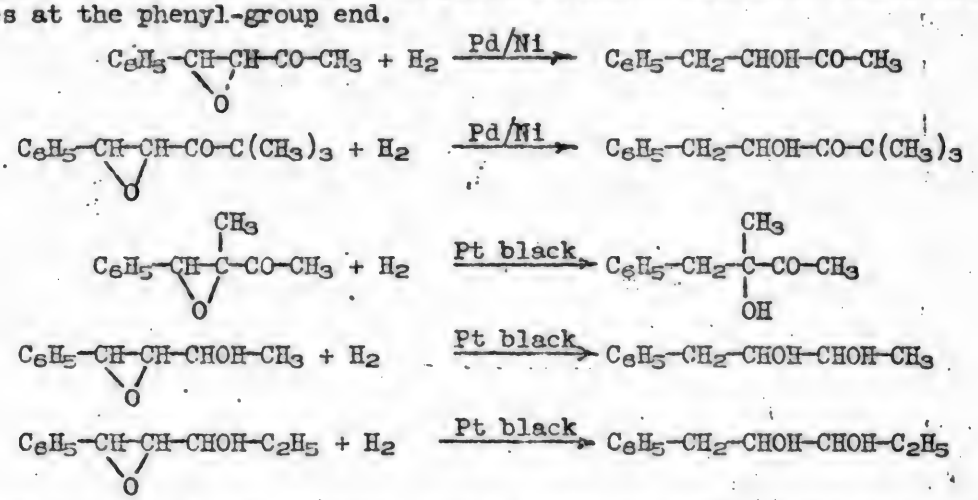
When Pt and Pd catalysts prepared by identical methods were used, the rate of absorption of hydrogen was about the same (a maximum when Pd/Ni was used in alcohol).

A difference in the catalytic properties of Pt and Pd had been often observed earlier, but in all the instances described in the literature the difference in selectivity of the foregoing catalysts with respect to a given bond in the molecule or to a given step-by-step hydrogenation process has been noted.

Thus, tetraphenylethylene is not hydrogenated over Pt, but adds 1 mole of H_2 readily over Pd, forming tetraphenylethane [5]. In their study of the processes of hydrogenation of numerous acetylenic compounds, Y.S.Zalkind and his associates and S.V.Lebedev and his associates demonstrated that over Pt hydrogenation results in the formation of saturated compounds, whereas only ethylenic compounds are formed when Pd is used [6].

We have discovered a new difference between these two catalysts, namely, their ability to display catalytic activity at different bonds within the same molecule.

In conclusion, it may be of some interest to consider for a moment the problem of the order in which the ether bond is ruptured during hydrogenation. Comparison of the results of our previous research with those in this paper indicates that the oxide ring in aliphatic-aromatic α-ketonic ethers always ruptures at the phenyl-group end.



The problem of the sequence in which various reagents are added to ethers has been discussed in the literature for a long time. A.A.Petrov showed that the sequence of rupture of an oxide ring depends on both the ether structure and the reagent involved [7]; for example, when alcohols are added to isobutylene ether, various ethers of isobutylene glycol are synthesized, depending on reaction conditions. In the presence of BF_3 tertiary ethers are obtained, whereas when alcoholates are used, we get primary ethers. His experimental results led A.A.Petrov to conclude that the acid or boron fluoride are formed with complex ethers – oxonium compounds that result in deformation of the ether bond; this opens the oxide ring on the side of the carbon atom having the

largest number of substituents. The action of the alcoholates does not involve deformation of the ether bond, being due to the fact that alcoholates react with ethers more readily than alcohols do. A.A.Petrov's hypothesis was further developed in his research on the addition of alcohols to divinyl ether [8], as well as in the work of American Chemists, notably Kadesh [9].

> A. A. Petrov showed that divinyl ether yields various ethers of erythritol when reacted with alcohols under various conditions. To explain these facts the author conjectured that the carbon atoms of the oxide ring have charges of different sign, but he cited no reason for this hypothetical distribution of charge; in particular, it is hard to understand why the terminal carbon atom, which is linked to an electronegative atom of oxygen, should have a negative charge.
>
> According to Kadesh, the reaction of ethers with the alcoholates are of the type of bimolecular nucleophilic substitutions at the carbon atom. The less substituted carbon atom, which possesses the least electron density, is subjected to the action of the alcoholate's ion. Kadesh proposes to call this type of reaction a "normal" reaction. When the rupture of the ether is occasioned by the catalytic action of hydrohalic acids, an abnormal reaction product is formed; the reaction is then "abnormal" according to Kadesh, and is of the type S_N^1; the monomolecular rupture of the oxide ring facilitates the resonance stabilization of the carbonium ion.

We cannot agree with Kadesh's hypothesis. We believe that both processes are normal reactions. The abnormal reactions are those in the transitional stages of which (in the reaction complex) substances are formed that are isomers of the expected ones, through intramolecular group reactions and electron shifts, owing to the fact that energy considerations favor a course of the process that is not provided for by structural theory [10].

In the case in question both processes are normal, since the substances formed in the addition of alcohols to ethers can be readily derived by using the principles of classical organic chemistry.

In all kinds of organic reactions we must expect that the process may follow one of two courses, depending upon what is the factor that causes the reaction:

1) The deformation of the molecule under the influence of the catalyst or the solvent;

2) The direct action of the reagent upon the initial molecule of the substance.

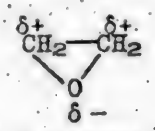
Of the basic reaction types: substitution, cleavage, and addition, only the first two have been clearly classified as reactions of Class I or II nucleophilic, electrophilic, and radical substitution or cleavage (S_N^1, S_N^2, E_N^2, etc), from the standpoint of electronic theory and kinetic processes. It is advisable to supplement the symbols adopted for substitution and cleavage reactions with other symbols to denote various kinds of addition reactions. These processes may also be classified as Class I and II nucleophilic, electrophilic, and radical reactions, and denoted by the following symbols: A_N^1, A_N^2, A_E^1, A_E^2, A_R^1, A_R^2 (Additio = addition), depending upon the nature of the active reagent.

Addition reactions to double and triple carbon-carbon bonds should be classed as of the A_E type; addition reactions to multiple bonds, conjugated

with a carbonyl or carboxyl group, are of the A_N type.

It is advisable to consider that the addition of various substances to ethers are addition reactions and not substitution reactions, as Kadesh does.

The structure of ethylene oxide may be represented as follows in the symbols of electronic concepts:

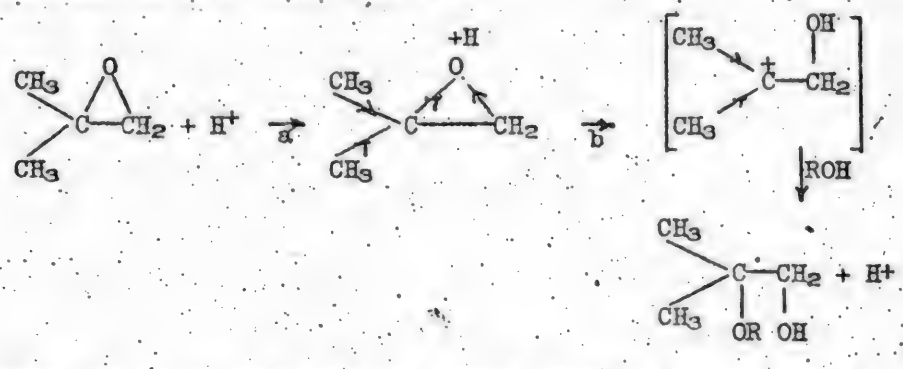


The existence of fractional positive charges on the carbon atoms whose link to the oxygen atom is broken when the oxide ring is ruptured governs the nucleophilic nature of the processes of addition to α-ethers (A_N type).

It is evident that when substituents are present, the state of the bonds in the oxide ring will depend upon the electron characteristics of the groups. With positive groups, supplying electrons, the C–O bond will be more polar and more polarizable under the action of a catalyst – an acid or BF_3, the converse holding true for negative groups. In that case, when the addition of a nucleophilic reagent precedes the deformation of the oxide ring, the bond that is more polarized under the catalyst's action (type A_N) is the one that ruptures.

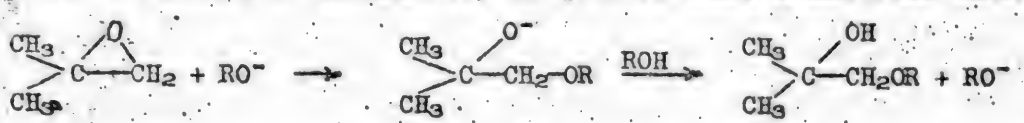
And if the rupture of the oxide ring takes place directly under the influence of a nucleophilic reagent (an anion or molecule possessing a pair of free electrons), the C–O bond in which the carbon atom has a large positive charge and hence a lower electron density (type A_N^2) will be the one that ruptures. In the last case, the steric factor ought to play an important part.

These considerations can be illustrated in the example already cited. In an acid medium what takes place is:



When the coordination of the proton with the oxygen takes place at high velocity, the reaction velocity is determined by the b stage. Substituents that possess +J and +M effects facilitate the rupture of the oxide bond; in this case the +M effect is more important, as is indicated by the data on the rupture of the oxide ring in divinyl ether [11].

Under the action of alcoholates, the process takes a different turn:



In this case, the more electrons are supplied by the substituents, the

Table 1

Hydrogenation of Benzalacetone Ether Over Pd

Test No.	Catalyst	Amount of catalyst, g	Solvent	Experimental conditions: pressure, mm. temperature, in °C	Quantity of substance to be hydrogenated, g	Quantity of hydrogen (in ml)		Time, in min., for absorption of 1 mole H	Rate of hydrogen absorption (ml per minute)		Yield of ketol, %
						Required (1 mole)	Absorbed		Initial (maximum)	Terminal	
11	Ni + $PdCl_2 \cdot 2NaCl$	1 g + 0.1 g	30 ml ethyl alcohol	765; 19°	1.5	220.6	229.7	11	41.5 (3)*	0.1	80
14	$PdCl_2 \cdot 2NaCl$	0.05	30 ml ethyl alcohol	766.8; 15°	0.78	113.7	118.5	15	34.5 (1)	0	72
15	Continuation of Exp. No.14 - added	-	20 ml ethyl alcohol	766.8; 15°	1.56	227.4	237.5	120	6 (3)	0.2	
19	Ni + $PdCl_2 \cdot 2NaCl$	1 g + 0.1 g	30 ml ether + 40 ml ethyl alcohol	770; 17°	3.24	470	464	70	49 (2)	0.75	72
16	Pd-black	0.1 g	70 ml ethyl alcohol	758; 17.5°	4.89	770	758	36	36 (3)	2.7	63
18	Pd-black	0.066	60 ml ether	743.5; 16°	3.24	485	388	385	3.0 (4)	2.5 ml per hr.	68

* The figures in parentheses indicate the time in minutes after the beginning of hydrogenation at which the hydrogen was absorbed at the maximum rate.

Table 2

Hydrogenation of Benzalacetone Ether Over Pt

Test No.	Catalyst	Amount of catalyst, g	Solvent	Experimental conditions: pressure, mm; temperature, in °C	Quantity of substance to be hydrogenated, g	Quantity of hydrogen (in ml)		Time, in min. for absorption of 1 mole H	Rate of hydrogen absorption (ml per minute		Semicarbazone
						Required (1 mole)	Absorbed		Initial (maximum)	Terminal	
1	Ni + H_2PtCl_6	1 g + 0.1 g	20 ml ethyl alcohol	767.5; 17°	1.6	236	249.5	105	20 (3)	0.7	not formed
2	Ni + H_2PtCl_6	2 g + 0.19 g	50 ml ethyl alcohol	771.7; 16°	3.2	467	472	125	39 (3)	1.0	not formed
5	Ni + H_2PtCl_6 + HCl	1.5 g + + 0.15 g + + 0.5 ml	100 ml ethyl alcohol	741.3; 17.5°	6.24	948	980	*	-	0.5	m.p. 149-154°**
6	Pt-black	0.1045 g	40 ml abs. ethyl alcohol	743.2; 14°	3.24	482	482	340	5.5 (2)	1.0	not formed
7	Pt-black	0.)580 g	60 ml ethyl alcohol	766; 13.5°	3.24	467	487	120	9.5	2.0	not formed

* The experiment took very long, totaling some 25 hours.

** The m.p. of the semicarbazone was 168-169° after the hydrogenation product had been hydrated (cf. Experimental Section).

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more are the positive charges neutralized and the lower is the electrophilia of the carbon atom surrounded by these substituents.

In the catalytic hydrogenation of α-ketonic ethers and ethers of unsaturated alcohols, the rupture of the oxide bond always takes place (p. a 542) at the phenyl end (substituent with a +M effect). The presence of a carbonyl or carboxyl group, i.e., of substituents possessing negative electron effects, on the other hand, ensures a more stable C–O bond in the oxide ring with regard to rupture during hydrogenation.

It follows from the foregoing that in this reaction the more highly polar bond ruptures more readily. It may therefore be stated that the hydrogenation reaction is governed by an ionic mechanism; this hypothesis is supported by the observation of the catalytic action of an acid (HCl) in the hydrogenation of compounds containing the C–O [4] and C–N [4] groups and an α-oxide ring.

EXPERIMENTAL

The benzalacetone ether was prepared by the method described by T.I. Temnikova and V.F.Martynov [1] and possessed the following constants: b.p. 124–126° at 10 mm; m.p. 55.5–56°.

I. Hydrogenation of Benzalacetone Ether Over Pd (Table 1).

Hydrogenation over Pd/Ni was effected as in our previous research [2]. Hydrogen was blown through the "duck" containing an alcoholic (or ether) solution of benzalacetone ether and 1 g of Ni, after which 1 ml of a solution of $PdCl_2 \cdot 2NaCl$ (0.1 g per ml H_2O) was added, and the rocker motor was started; this instant was taken as the start of the hydrogen process. Readings of absorbed hydrogen were made every minute.

We give below the course of hydrogenation by way of supplement to Table 1.

Experiment 11. Used: 1.5 g of benzalacetone ether; 30 ml of ethyl alcohol; 1 g of Ni; and 0.1 g of $PdCl_2 \cdot 2NaCl$; p = 765 mm; t = 19°.

T	2	4	6	8	10	15	20	25
V	82.8	164.5	214.4	218.75	219.05	221.50	222.10	222.6
v	82.0	82.5	49.9	4.35	0.35	2.45	0.6	0.50 etc.

Where: T = time in minutes, from start of hydrogenation;

V = quantity of hydrogen, in milliliters, absorbed in time T;

v = quantity of hydrogen, in milliliters, absorbed since the previous reading.

Corrections for the absorption of hydrogen by the catalyst were made in accordance with the specifications of Ginsberg and Ivanov [15].

Recovery of the hydrogenation product was effected in the same manner in all experiments where alcohol was the solvent.

The catalyst was filtered out in a Gooch filter. The alcohol was driven off in vacuum, and the residue dissolved in ether. The ether extract was washed with water and dried, and the ether driven off (all these driving-off operations were performed in a current of CO_2). The residue was distilled in vacuum.

In every instance, the principal fraction distilled at 96° and 1 mm (98°

at 1.5 mm); the fractions that boiled at lower and higher temperatures were extremely small. The yield of the ketol was as high as 80%.

d_4^{19} 1.0853; n_α^{19} 1.52403; MR_α 46.22.

$C_{10}H_{12}O$ 0' F$_g$. Calculated: MR 46.12.
0.2036 g substance: 0.5445 g CO_2; 0.1364 g H_2O.
0.0648 g substance: 0.1734 g CO_2; 0.0431 g H_2O.
Found %: C 72.94, 72.93; H 7.49, 7.45.
$C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.38.

The semicarbazone was synthesized by mixing the substance with a water-alcohol solution of semicarbazide acetate. The mixture warms up at first, and soon crystals begin to settle out, soon filling the whole solution. The yield is nearly quantitative. Recrystallization from alcohol yields colorless acicular crystals with a m.p. of 169-170°.

0.1232 g substance: 20.25 ml N_2 (16°, 755 mm).
Found %: N 19.08.
$C_{11}H_{15}N_3O_2$. Calculated %: N 19.05.

The phenylosazone was prepared by heating a mixture of 0.55 g of the substance with 1.22 g of phenylhydrazine in 15 ml of 30% acetic acid for 5 hours over a water bath. After four recrystallizations from ethyl alcohol we got pale golden, lamellar crystals with a m.p. of 171-173°.

0.1026 g substance: 14.2 ml N_2 (18°, 769.8 mm).
Found %: N 16.34.
$C_{22}H_{22}N_4$. Calculated %: N 16.37.

We were unable to synthesize a crystalline derivative by means of a reaction with naphthyl isocyanate.

Quantitative Determination of the Percentage of α-Ketol By Means of Fehling's Solution [12]

This determination was performed in parallel in two Erlenmeyer flasks (200 ml), fitted with reflux condensers. A mixture of 10 ml of a $CuSO_4$ solution (69.28 g per liter), 10 ml of an alkaline solution of Rochelle salt (344 g + +100 g of NaOH per liter), and 20 ml of water was heated for 10 minutes. An ampoule with a weighed quantity of the ketol had been placed in one of the flasks in advance. When the reaction was over, the flasks were cooled with jets of water, and 10 ml each of 30% KI and 25% H_2SO_4 were added. The iodine that separated out was titrated back with hyposulfite in the presence of starch.

1) 0.1012 g substance; required 12.2 ml 0.1N hyposulfite solution (blank test = 25.15 ml hyposulfite). Computed: 95.33% ketol in weighed batch.

2) 0.2318 g substance; required 26.3 ml 0.1N hyposulfite solution (blank test = 50.30 ml hyposulfite). Computed: 94.23% ketol in weighed batch.

Determination of Changeability of the α-Ketol in Alkaline Media

A weighed batch of 0.0776 g of the substance was boiled for 10 minutes with an alkaline solution of Rochelle salt (10 ml), after which 10 ml of $CuSO_4$ solution was added; the rest of the determination was as described above.

Back titration of the I_2 required 18.3 ml of 0.1N hyposulfite solution, corresponding to 73.56% of the ketol.

Synthesis of α-Methyl-α-phenyl-β-benzylethylene Glycol

A solution of 3 g of the ketol in absolute ether was added drop by drop,

with ice-water chilling and stirring, to an ether solution of C_6H_5MgBr, prepared with 1.5 g of Mg. The mixture was then set aside to stand overnight, after which it was heated to the boiling point of ether for 3 hours. The organomagnesium compound was decomposed with water, and the ether layer separated and desiccated over $MgSO_4$. After the ether was driven off, we got a white crystalline substance. Recrystallization from ligroin (80-100°) yielded colorless, acicular crystals with a m.p. of 108.5-109.5°

0.1146 g substance; 0.3328 g CO_2; 0.0782 g H_2O.
0.1258 g substance; 0.3650 g CO_2; 0.0850 g H_2O.
Found %: C 79.15, 79.18; H 7.64, 7.56.
$C_{16}H_{16}O_2$. Calculated %: C 79.30; H 7.48.

The glycol was oxidized with chromic trioxide by the method described earlier [13]: 1.2 g of the glycol, 3.2 g of $KHSO_4$ in 10 ml of H_2O, and 0.8 g of CrO_3 in 4 ml of H_2O. The usual treatment resulted in the recovery of acetophenone as its semicarbazone with a m.p. of 198-199°.; it exhibited no depression when fused with a known sample of acetophenone semicarbazone. The only acid product recovered was benzoic acid, identified by its melting point; a test sample mixed with known benzoic acid fused at 121°.

II. Hydrogenation of Benzalacetone Ether Over Pt (Table 2)

This hydrogenation was performed like those in all our preceding experiments, in the apparatus designed by Academician S.V. Lebedev [14] as a "duck".

Hydrogenation proceeded as follows:

Experiment 1. 1.6 g of benzalacetone ether; 20 ml of ethyl alcohol; 1 g of Ni; and 0.1 g of H_2PtCl_6; p = 767.5; t = 17°.

T	1	2	3	4	5	6	7	8	9	10	15	20	25	30
V	4	15	35	51	63	70	77	83	88	93	117.5	129.0	142.0	152.5
v	4	11	20	16	12	7	7	6	5	5	21.5	14.5	13.0	10.5
										average per minute..	4.3	2.9	2.6	2.1

After removal of the catalyst and the usual treatment, the hydrogenation products of Experiments 1 and 2 (Table 2) were recovered and subjected to distillation together in a 3-mm vacuum.

Fraction I: 90-101° 0.5 g,
Fraction II: 102-115° 0.86 g,
Fraction III: 120-135° 0.73 g.

The residue was a tarry mass that solidified upon cooling.

The semicarbazone synthesized from Fraction I had a m.p. of 141° and caused no depression when mixed with the semicarbazone of benzalacetone ether; we synthesized an insignificant quantity of the same carbazone from Fraction II.

Experiment 5. Used: 6.24 g of benzalacetone ether; 100 ml of ethyl alcohol; 1.5 g of Ni; 3 ml of a 5% solution of H_2PtCl_6; and 0.5 ml of HCl; p = 771.7; t = 16°.

Fractionation of the hydrogenation products in vacuum at 2-2.5 mm yielded the following fractions:

Fraction I: 87-90° 0.17 g,
Fraction II: 91-98° 0.42 g,

Fraction III: 100-106° 1.34 g,
Fraction IV: 106-110° 1.82 g
V: Residue — tar.

The semicarbazone was synthesized from Fraction II. M.p. after recrystallization from alcohol = 137-144°.

After 3 days of standing, large crystals (3 x 12 x 1 mm) settled out as prisms, which proved to be benzalacetone ether, m.p. 55-56°; a mixed test sample exhibited no depression.

The liquid portion of Fractions III and IV was fractionated in a 1-mm vacuum after the above-mentioned crystals had been removed:

Fraction I: up to 94°.
Fraction II: 94-96°.

The semicarbazone of Fraction II, recrystallized from alcohol, had a m.p. of 149-154°; a test sample mixed with the semicarbazone of benzylacetylcarbinol (m.p. = 169-170°) fused at 157-160°.

0.9 g of the fraction with a b.p. of 94-96° at 1 mm was hydrated in 100 ml of 5% H_2SO_4, with stirring, for 30 minutes and heated to 50°.

Then the ether extract was made of the solution, which had been neutralized with potash. After it had been desiccated and the ether had been removed, there remained a slightly yellowish substance with an extremely small quantity of white crystals, which were filtered out. There was 0.32 g of the liquid substance, from which 0.35 g of the semicarbazone was prepared; it had a m.p. of 166-168° and 168-169° after a second recrystallization.

A test sample exhibited no depression when mixed with the semicarbazone of benzylacetylcarbinol.

SUMMARY

1. The differing selectivity of the hydrogenation of benzalacetone ether in the presence of Pt and Pd has been demonstrated. When a platinum catalyst (Pt black, Pt/Ni) is used, the carbonyl group is reduced, and an oxide of an unsaturated alcohol — methylstyrylcarbinol ether — is formed.

When a palladium catalyst (Pd black, Pd/Ni) is used, the oxide ring is ruptured and an α-ketol — benzylacetylcarbinol — is formed.

2. Comparison of the results of this research and of preceding investigations disclosed a general rule, observable in the hydrogenation of the α-ethers of unsaturated ketones and the α-ethers of unsaturated alcohols of the aliphatic-aromatic series: the oxide ring is always ruptured at the side nearest the phenyl group.

3. General considerations have been set forth regarding the classification of reactions, and electronic symbols have been proposed to denote addition reactions (type A).

4. The addition reactions of alcohol to alpha ethers are nucleophilic. If the addition of the reagent precedes the deformation of the oxide ring by acids, the reaction rate is governed by the velocity of rupture of the oxide ring; the reaction is monomolecular (type A_N^1).

If the addition of the oxide is effected by the direct action of the nucleophilic reagent, the reaction is bimolecular (type A_N^2).

LITERATURE CITED

[1] T.I.Temnikova and V.F.Martynov, J. Gen. Chem., 15, 499 (1945).

[2] T.I.Temnikova and V.A.Kropachev, J.Gen. Chem., 18, 692 (1948).

[3] H. Muller and H.V.Pechmann, Ber., 22, 2127 (1889).

[4] T.I.Vekhotko, J. Gen. Chem., 11, 99, 103 (1941); W. Hartung, J. Am. Chem. Soc., 53, 2248 (1931).

[5] N.K.Yurashevsky, J. Gen. Chem., 8, 438 (1938); Y. S. Zalkind and Assoc., J. Gen. Chem. 3, 91 (1933); 7, 470, 1235 (1937).

[6] S.V.Lebedev, A.I.Gulyayeva, and A.A.Vasilyev, J. Gen. Chem., 5, 1421 (1935).

[7] A.A.Petrov, J. Gen. Chem., 14, 1038 (1944); 10, 991 (1940).

[8] A.A.Petrov, Dokl.USSR. Acad. Sci., 50, 249 (1945); J. Gen. Chem., 16, 1627 (1946).

[9] K. Kadesh, J. Am. Chem. Soc., 68, 41, (1946).

[10] E.g., T.I.Temnikova, J. Gen. Chem., 10, 469 (1940); 15, 518 (1945); T.I.Temnikova and E.I.Kulachkova, J. Gen. Chem., 19, 1324 (1949).

[11] A.A.Petrov, J. Gen. Chem., 11, 991 (1941).

[12] G. Meier. Analysis and determination of the structure of organic compounds, 1935, p 453.

[13] A.E.Favorsky and T.I.Temnikova, J. Gen. Chem., 4, 754 (1934).

[14] S.V.Lebedev. Life and Works. GNTI, 1938, p.381.

[15] A.S.Ginsberg, J. Gen. Chem., 5, 795 (1935).

Received March 17, 1948.

THE SACCHARIN REARRANGEMENT OF THE DISACCHARIDES

IV. ISOMERIZATION OF GLUCOSIDO-3-GLUCOSE TO BIOSACCHARINIC ACID

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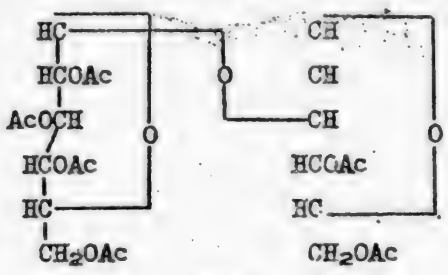
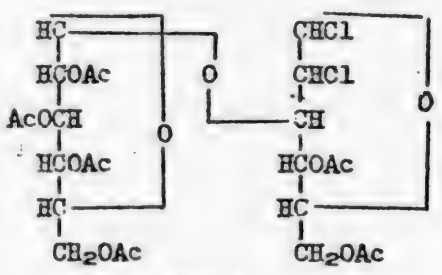
In our previous paper [1] we studied the isomerization of maltose to maltosaccharinic acid. The present paper is devoted to the analogous rearrangement of glucosido-3-glucose.

Glucosido-3-glucose was converted into hexacetylglucosido-3-glucal (I) via the octacetate and a bromine derivative. Passing anhydrous chlorine through a chloroform solution of hexacetylglucosido-3-glucal yielded 1,2-dichlorohexacetylglucosido-3-glucose (II), which is readily convertible into monochlorohexacetylglucosido-3-glucose (III) by the action of wet silver carbonate. Boiling the latter compound with lead oxide converts it into glucosido-3-glucosaccharinic acid (IV).



(I)



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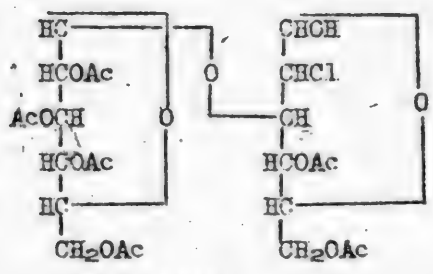

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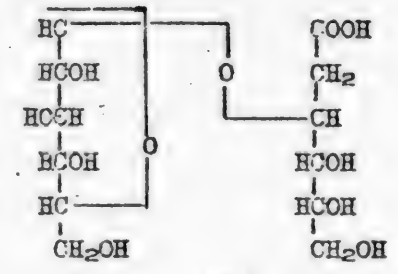

(IV)

The acid was identified through its derivatives: the calcium and barium salts, the phenylhydrazide, and the methyl ester.

EXPERIMENTAL

1. Hexacetylglucosido-3-glucal

200 ml of 60% acetic acid was poured over 30.5 g of acetobromoglucosido-3-glucose (m.p. 162°, $[\alpha]_D^{20}$ + 11.8°, in chloroform); 40 g of zinc dust was a

added, and the mixture was agitated mechanically for 2 hours. The solution was then diluted with 500 ml of water, and the reaction product was triply extracted with chloroform. The chloroform solution was washed, dried, and evaporated. The syrup obtained after the chloroform had been evaporated crystallized rapidly. The substance was purified by recrystallization from alcohol. The yield was 17.2 g, or 78% of theory.

M.p. 109°; $[\alpha]_D^{20}$ + 18.4° (in chloroform).

0.1684 g substance: 17.8 ml 0.1N NaOH solution.
0.1619 g substance: 17.3 ml 0.1N NaOH solution.
Found %: $COCH_3$ 45.81, 46.18
$C_{24}H_{32}O_{15}$. Calculated %: $COCH_3$ 46.07.
0.0521 g substance: 16.1 ml bromine solution, T = 0.0009.
0.0620 g substance: 20.2 ml bromine solution, T = 0.0009.
Found %: Br 21.84, 22.45.
$C_{24}H_{32}O_{15}Br_2$. Calculated %: Br 22.22.

2. α-Glucosido-2-arabic Acid

6.5 g of hexacetylglucosido-3-glucal was dissolved in 100 ml of glacial acetic acid, and a current of oxygen, containing 3-5% of ozone, was passed through the solution. After oxidation was complete (bromine-water test), the solution was diluted with 300 ml of ether, 60 g of zinc dust was added, and the whole was heated, with stirring, over a water bath in a flask fitted with a reflux condenser. The ether layer was separated from the acetic-acid layer, was washed, desiccated, and evaporated to dryness. The residue was dissolved in ethyl alcohol and left to stand in a cool place. The hexacetyl-α-glucosido-2-arabinose gradually crystallized. The crystals were filtered out and recrystallized from ethyl alcohol for purification. The yield was 4.4 g, or 69% of theory.

M.p. 142°; $[\alpha]_D^{20}$ + 25.8° (in chloroform).
0.1149 g substance: 12.3 ml 0.1N NaOH solution.
0.1302 g substance: 14.4 ml 0.1N NaOH solution.
Found %: $COCH_3$ 45.24, 46.09.
$C_{23}H_{32}O_{16}$. Calculated %: $COCH_3$ 45.74.

4.1 g of hexacetylglucosido-2-arabinose was dissolved in 100 ml of absolute alcohol. After the solution had been chilled, a chilled solution of sodium alcoholate (1.1 g of sodium in 100 ml of alcohol) was added. The mixture was vigorously agitated mechanically for 1 hour, after which it was poured into 150 ml of water. The solution, neutralized with acetic acid, was evaporated to a small volume in vacuum. The residue was dissolved in 300 ml of bromine water and left exposed to light for 3 days. After the solution had been boiled and neutralized with calcium carbonate, it was evaporated to small volume. When absolute ethyl alcohol was gradually added to the solution, flakes of calcium glucosido-2-arabinate precipitated out.

0.1704 g substance: 0.0154 g CaO.
0.2272 g substance: 0.0187 g CaO.
Found %: Ca 5.86, 6.04.
$(C_{11}H_{19}O_{11})_2Ca$. Calculated %: Ca 5.77.

3. Glucosido-3-(2-desoxy)-glucose, 2-Desoxy-glucosido-3-gluconic Acid

6.4 g of glucosido-3-glucal (m.p. 160-162°), obtained by saponifying the hexacetate, was dissolved in 300 ml of a 3% solution of sulfuric acid, and the solution thus prepared was set aside to stand at room temperature for 2 days.

After the solution had been neutralized with barium carbonate, it was evaporated in vacuum until it turned into a thick syrup. The syrup was mixed with absolute ethyl alcohol and left to stand in a porcelain dish.

The glucosido-3-(2-dexoxy)-glucose gradually crystallized. The yield was 5.1 g, or 77% of theory.

M.p. 188°; $[\alpha]_D^{20}$ + 22.6° (in water).

0.0560 g substance: 0.0908 g CO_2; 0.0326 g H_2O.
0.0927 g substance: 0.1442 g CO_2; 0.0619 g H_2O.
Found %: C 44.70, 43.95; H 6.29, 6.47.
$C_{12}H_{22}O_{10}$. Calculated %: C 44.30; H 6.75.

The phenylhydrazone of glucosido-3-(2-desoxy)-glucose prepared by reacting phenylhydrazine with the glucosido-3-(2-desoxy)-glucose in the presence of ethyl alcohol and acetic acid, has a m.p. of 180-181°.

0.1004 g substance: 6.1 ml N_2 (16°, 730 mm).
0.1214 g substance: 7.6 ml N_2 (16°, 730 mm).
Found %: N 6.82, 6.98.
$C_{18}H_{28}N_2O_9$. Calculated %: N 6.74.

Heating glucosido-3-(2-desoxy)-glucose with acetic anhydride in the presence of anhydrous sodium acetate yielded heptacetylglucosido-3-(2-desoxy)-glucose, with a m.p. of 175-176°.

0.0840 g substance: 11.1 ml 0.1N NaOH solution.
0.1109 g substance: 14.4 ml 0.1N NaOH solution.
Found %: $COCH_3$ 48.69, 48.92.
$C_{28}H_{36}O_{17}$. Calculated %: $COCH_3$ 48.55.

2.8 g of glucosido-3-(2-desoxy)-glucose was dissolved in 300 ml of bromine water, and the solution was set aside to stand in the light for two days, with frequent stirring. Then the boiling solution was neutralized with calcium carbonate and filtered. When absolute ethyl alcohol was gradually added to the concentrated solution, flakes of the calcium salt of glucosido-3-(2-desoxy)-gluconic acid settled out. The precipitate was filtered out, washed, and dried.

0.0825 g substance: 0.0058 g CaO.
0.1147 g substance: 0.0092 g CaO.
Found %: Ca 4.98, 5.72.
$(C_{12}H_{21}O_{11})_2Ca$. Calculated %: Ca 5.54.

When the calcium salt of glucosido-3-(2-desoxy)-gluconic acid was precipitated with the calculated quantity of oxalic acid and the filtered solution was then evaporated to a thick syrup, the lactone of glucosido-3-(2-desoxy)-gluconic acid was synthesized. The syrup crystallized after a few days.

M.p. 131-132°; $[\alpha]_D^{20}$ + 42.4° (in water).

0.0904 g substance: 0.1464 g CO_2; 0.0481 g H_2O.
0.1340 g substance: 0.2189 g CO_2; 0.0765 g H_2O.
Found %: C 44.92, 44.67; H 5.92, 6.35.
$C_{12}H_{20}O_{10}$. Calculated %: C 44.44; H 6.17.

4. 1,2-Dibromohexacetylglucosido-3-glucose

2.4 g of hexacetylglucosido-3-glucal was dissolved in 100 ml of anhydrous chloroform, and a chloroform solution of bromine was added to the chilled solution until color appeared. The solution was set aside for 3 days, and whenever it was decolored, more of the chloroform solution of bromine was added. The solution was then evaporated to minimum value, and the residue was mixed with

solution was then evaporated to minimum value, and the residue was mixed with petroleum ether. The 1,2-dibromohexacetylglucosido-3-glucose gradually crystallized. The substance was purified by recrystallization from a 1:5 mixture of ethyl alcohol and amyl alcohol. The yield was 2.2 g, or 73% of theory.

M.p. 159°; $\underline{l}$ = 0.5; c = 0.45; $[\alpha]_D^{20}$ + 10.09°; $[\alpha]_D^{20}$ + 44.8° (in chloroform).

0.1062 g substance: 0.0549 g AgBr.
0.1389 g substance: 0.0705 g AgBr.
Found %: Br 21.98, 21.64.
$C_{24}H_{32}O_{15}Br_2$. Calculated %: Br 22.22.

1,2-Dibromohexacetylglucosido-3-glucose dissolves in chloroform, ethyl acetate, tetrachloroethane, and ethyl alcohol. It turns black in air, evolving hydrogen bromide.

5. 1,2-Dichlorohexacetylglucosido-3-glucose

12.5 g of hexacetylglucosido-3-glucose was dissolved in 200 ml of anhydrous chloroform, and a current of anhydrous chlorine was passed through the chilled solution. After the reaction was complete (bromine water test), the solution was evaporated to small volume. Gradual addition of petroleum ether to the residue caused crystals of 1,2-dichlorohexacetylglucosido-3-glucose to settle out. This substance was purified by double recrystallization from a 1:5 mixture of ethyl and amyl alcohols. The yield was 11.2 g, or 79% of theory.

M.p. 161-162°; $\underline{l}$ = 0.5; c = 0.4; α + 10.84°; $[\alpha]_D^{20}$ + 54.2° (in tetrachloroethane).

0.0959 g substance: 0.0556 g AgCl.
0.1121 g substance: 0.0515 g AgCl.
Found %: Cl 11.95, 11.49.
$C_{24}H_{32}O_{15}Cl_2$. Calculated %: Cl 11.25.

1,2-Dichlorohexacetylglucosido-3-glucose dissolves in chloroform, acetone, ethyl acetate, and tetrachloroethane. Exposure to air does not decompose it.

6. Mono-2-chlorohexacetylglucosido-3-glucose

10.8 g of 1,2-dichlorohexacetylglucosido-3-glucose was dissolved in 150 ml of anhydrous chloroform, 5.8 g of wet silver carbonate was added, and the solution was then agitated mechanically for 5 hours.

After the reaction was complete (bromine-water test), the solution was filtered and evaporated to small volume. Mixing the residue with petroleum ether caused crystals of mono-2-chlorohexacetylglucosido-3-glucose to settle out. The substance was purified by recrystallization from ethyl alcohol. The yield was 7.8 g, or 75% of theory.

M.p. 169°; $\underline{l}$ = 0.5; c = 0.42; α + 8.3°; $[\alpha]_D^{20}$ + 39.8° (in chloroform).

0.0702 g substance: 0.0163 g AgCl.
0.0998 g substance: 0.0249 g AgCl.
Found %: Cl 5.82, 6.23.
$C_{24}H_{33}O_{18}Cl$. Calculated %: Cl 5.79.

7. Glucosido-3-glucosaccharinic acid

7.6 g of mono-2-chlorohexacetylglucosido-3-glucose was dissolved in 50 ml of chloroform. 400 ml of water and 30 g of freshly prepared lead oxide were added to the solution, which was then heated over a water bath for 30-35 hours

(halogen test) with constant stirring in a flask fitted with a reflux condenser. At first, the temperature of the water bath was kept at 60-80°; it was raised to 90-100° toward the end. The filtered solution was washed with water. The precipitate was suspended in water, the lead being thrown down with hydrogen sulfide. The solution was filtered, heated to remove the hydrogen sulfide, and then combined with the principal water-chloroform solution. The combined solution was evaporated to dryness, the reducing substance being leached out of the residue with organic solvents. The precipitate was dissolved in water, and a current of hydrogen sulfide was again passed through the solution. The filtered solution was heated with calcium carbonate. The solution was filtered to remove the excess calcium carbonate and then evaporated to small volume. The gradual addition of absolute ethyl alcohol to the remaining concentrated solution caused flakes of the calcium salt of glucosido-3-glucosaccharinic acid to settle out. The yield was 4.1 g, or 79% of theory.

0.0721 g substance: 0.0058 g CaO.
0.1008 g substance: 0.0085 g CaO.
Found %: Ca 5.82, 5.99.
$(C_{12}H_{21}O_{11})_2Ca$. Calculated %: Ca 5.54.

Decomposition of the calcium salt of glucosido-3-glucosaccharinic acid with a computed quantity of oxalic acid and subsequent evaporation of the filtered solution yielded a syrup of the lactone of glucosido-3-glucosaccharinic acid. When the syrup was mixed with absolute alcohol, it crystallized after several days elapsed. B.p. 131-132°; $[\alpha]_D^{20}$ + 42.1° (in water). A test sample caused no depression when mixed with glucosido-3-(2-desoxy)-gluconic acid. The yield of the lactone was 2.8 g, or 72% of theory.

0.0949 g substance: 0.1545 g CO_2; 0.0513 g H_2O.
0.1203 g substance: 0.1972 g CO_2; 0.0648 g H_2O.
Found %: C 44.55, 44.92; H 5.98, 6.01.
$C_{12}H_{20}O_{10}$. Calculated %: C 44,44; H 6.17.

The m.p. of the phenylhydrazide of glucosido-3-glucosaccharinic acid is 178-180°.

0.0848 g substance: 5.4 ml N_2 (19°; 730 mm).
0.1017 g substance: 6.2 ml N_2 (19°, 730 mm).
Found %: N 7.01, 6.83.
$C_{18}H_{32}N_2O_{10}$. Calculated %: N 6.45.

8. Methylation and Hydrolysis of Glucosido-3-glucosaccharinic Acid

The acid was methylated by dimethyl sulfate in the presence of an alkali. 10.4 g of the calcium salt of glucosido-3-glucosaccharinic acid yielded 8.9 g of the methylated product, or 68% of theory.

n_D^{20} 1.4987; $[\alpha]_D^{20}$ + 12.5° (in chloroform).
0.0522 g substance: 0.2115 g AgI.
0.0702 g substance: 0.2835 g AgI.
Found %: OCH_3 54.19, 54.09.
$C_{20}H_{38}O_{11}$. Calculated %: OCH_3 54.82.

Boiling methylated saccharinic acid with a dilute solution of sulfuric acid yielded methylated glucosaccharinic acid and a methylated glucose. After the solution had been neutralized with calcium carbonate and filtered, the methylated glucose was extracted with chloroform. Evaporation of the chloroform yielded crystals of 2,3,4,6-tetramethylglucose.

M.p. 91-93°; $[\alpha]_D^{20}$ + 83.8° (in ethyl alcohol) [3].

0.0626 g substance: 0.2475 g AgI.
0.0652 g substance: 0.2551 g AgI.
Found %: OCH_3 52.69, 52.38.
$C_{10}H_{20}O_8$. Calculated %: OCH_3 52.56.

The anilide of tetramethylglucose has a m.p. of 135-136° and $[\alpha]_D^{20}$ +232.4° (in acetone), which agrees with the published data [4].

After the tetramethylglucose had been removed, the solution was evaporated to small volume. The gradual addition of absolute ethyl alcohol to the concentrated solution caused flakes of the calcium salt of methylated ortho-glucosaccharinic acid to settle out.

The calcium salt was purified by converting it to the barium salt.

0.0642 g substance: 0.0261 g $BaSO_4$.
0.0789 g substance: 0.0319 g $BaSO_4$.
Found %: Ba 23.97, 23.80.
$(C_9H_{17}O_6)_2Ba$. Calculated %: Ba 23.68.

SUMMARY

1. Glucosido-3-(2-desoxy)-gluconic or glucosido-3-glucosaccharinic acid has been synthesized.

2. 1,2-Dichloro- and 1,2-dibromohexacetylglucosido-3-glucose, as well as mono-2-chlorohexacetylglucosido-3-glucose have been synthesized.

3. Oxidation of glucosido-3-glucal yields glucosido-2-arabinose.

LITERATURE CITED

[1] A Gakhokidze, J. Gen. Chem., 18, 60 (1948).

[2] A. Gakhokidze, J. Gen. Chem., 16, 1923 (1946).

[3] W. Haworth and assoc., J. Chem. Soc., 1927, 2809.

[4] H. Pringsheim, A. Steingroever, Ber., 59, 1001 (1926).

Received June 18, 1948.

SYNTHESIS OF KETONES FROM CYMENE AND THE FEASIBILITY OF UTILIZING THEM IN THE GRIGNARD SYNTHESIS OF ALCOHOLS

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Cymene has been attracting more and more attention of late from research workers owing to the fact that it is produced in considerable quantity as a by-product in the sulfite digestion of cellulose. According to Tumbin [1], 10 to 12 kg of sulfite oil, containing 70-80% cymene, are obtained from a ton of cellulose. Groggins [2] reports that in the USA as much as 3000 tons of cymene are recovered from sulfite turpentine. Thus, as a cheap material, cymene naturally attracts the attention of researchers, and the literature is full of papers on the nitration or sulfonation of cymene, as well as the synthesis of various dyestuffs from aminocymene. But some of the topics related to cymene still remain insufficiently explored. There is only one paper by Claus [3] on the synthesis of the ketones in the literature; he synthesized cymene ketones from cymene and the corresponding acid chlorides by means of the Friedel-Crafts reaction in a hydrogen-sulfide medium and in the presence of aluminum chloride. The synthesis of aceto-p-cymene by the Friedel-Crafts reaction in a hydrogen-sulfide medium is described in The Synthesis of Organic Preparations [4]. We resolved to work out the synthesis of cymene ketones without hydrogen sulfide in a medium using cymene in excess as a solvent. We synthesized the following ketones:

1) Aceto-p-cymene or 2-methyl-5-isopropylacetophenone, with a yield of 51.7% (the yield in a hydrogen-sulfide medium is below 50%).

2) 2-Butyro-p-cymene or 2-methyl-5-propylbutyrophenone, with a yield of 30% (the yield in a hydrogen-sulfide medium is below 25%).

3) 2-Isobutyro-p-cymene or 2-methyl-5-isopropylisobutyrophenone. The yield of the ketone is 24.6% (there are no figures on the yield of this ketone in the literature).

4) 2-Isovaleryl-p-cymene or 2-methyl-5-isopropylisovalerophenone, with a yield of 28.4%, whereas the yield does not exceed 18% in a hydrogen-sulfide medium.

5) Chloroaceto-p-cymene or 2-methyl-5-isopropylchloroacetophenone, with a yield of 30.2% (no yield is mentioned in the literature).

6) Lastly, we have synthesized for the first time 2-benzoyl-p-cymene or 2-methyl-5-isopropylbenzophenone, with a yield of 25.5%.

The ketones we synthesized have properties that fully correspond with those of the ketones described by Claus, which indicates that the ketone group entered the ortho position to the methyl-cymene radical even when no hydrogen sulfide was present. This was also corroborated by the oxidation of the ketones to methylisophthalic acid. With two of the ketones, namely, aceto-p-cymene and

isobutyro-p-cymene, we tried to synthesize alcohols, reacting these ketones with Grignard reagents prepared from ethyl bromide and ethyl iodide. But we got no reaction in either case; the unchanged ketone was recovered. Supposing that raising the temperature of the reaction mixture would bring about a reaction anyhow, we heated the mixture, after the ether had been driven off, for 2 hours at 110° in a toluene medium, but again failed to obtain a reaction. Thus, a Grignard reagent does not react with the ketones synthesized from cymene, probably because of steric hindrances.

EXPERIMENTAL

1. Synthesis of Aceto-p-cymene

For this synthesis we took 34 g of acetic anhydride (1/3 mole), 133 g of aluminum chloride (1 mole), and 200 g of cymene. The cymene and the aluminum chloride were placed in a flask with a reflux condenser, the mixture was chilled with ice, and the acetic anhydride was gradually added to the contents of the flask with constant stirring. After all the anhydride had been added, the mixture was heated for 5 hours over a boiling water bath until no more hydrogen chloride was evolved. Then the flask was cooled, and the coordination compound within it was decomposed with ice, hydrochloric acid being added to dissolve the basic salts of aluminum. The top layer, which constituted a solution of the ketone in cymene, was separated out, washed several times with water, and desiccated with calcium chloride. After desiccation, the cymene solvent was driven off at temperatures up to 180°, and the residue of 59 g was distilled in vacuum:

Fraction I: B.p. 100-125° at 6 mm .....23 g,
Fraction II: B.p. 125-127° at 6 mm .....30 g,
Residue (tar) . . . . . 5 g.

The first fraction is a mixture of cymene and the ketone, whereas the second is pure ketone, with a yield of 51.7%. The ketone is a colorless liquid with a pleasant aroma that reminds one of acetophenone: b.p. 247-249° at 756 mm and 125-127° at 6 mm:

n_D^{20} 1.502; d_{20}^{20} 0.9510; MR_D 54.50. $C_{12}H_{16}O$. Calculated: MR_D 54.02.

0.1098 g substance: 0.3276 g CO_2; 0.0942 g H_2O.
Found %: C 81.37; H 9.53.
$C_{12}H_{16}O$. Calculated %: C 81.82; H 9.16.

Reacting it with hydroxylamine hydrochloride in the presence of sodium acetate yielded the oxime as a thick oil that did not crystallize upon cooling nor after prolonged standing. Oxidizing the ketone by heating it with potassium permanganate in an alkaline medium yielded 1-methylisophthalic acid, with a m.p. of 332°, identified by its characteristic properties [3] (the m.p. of this acid is cited as 330-332°). Besides the 1-methylisophthalic acid, a small quantity of 1-methyl-4-isopropylphenylglyoxylic acid, a viscous yellow oil, was formed during oxidation (Claus also found that this acid is formed as a by-product in the oxidation of aceto-p-cymene). Oxidation of the ketone by heating it with concentrated nitric acid yielded 1,2,4-trimellitic acid [5] with a m.p. of 228°. (The m.p. given in the literature is 228°).

We synthesized this same ketone by reacting acetyl chloride (39 g) with 200 g of cymene in the presence of 65 g of aluminum chloride. The method of synthesizing the ketone with acetyl chloride does not differ from that described above. Fractionation yielded 47 g of the ketone with a m.p. of 247-259°. Thus, here the yield of the ketone is 55% of theory.

In the literature the following constants are cited for aceto-p-cymene: B.p. 248-250°; d^{0} 0.9713; d^{15} 0.9715; d^{20} 0.956.

2. Synthesis of 2-Butyro-p-cymene

For this synthesis we took 45 g of butyryl chloride, 55 g of aluminum chloride, and 230 g of cymene (the excess serving as a solvent). Synthesis was effected as in the first experiment. After the excess cymene had been driven off, the residue was fractionated in vacuum:

Fraction I: B.p. 100-155° at 12 mm ..... 31 g,
Fraction II: B.p. 158-160° at 12 mm ..... 25 g,
Residue (tar) ..... 4 g.

The first fraction was a mixture of the ketone and cymene, whereas Fraction 2 was the ketone proper. The yield of the ketone was 30.0% (in terms of the acid chloride). The ketone is a liquid with a pleasant aroma. It boils at 264-266° at atmospheric pressure (265-266° according to the literature [3]):

n_D^{15} 1.513; d_{15}^{15} 0.945; MR_D 63.54; $C_{14}H_{20}O$. Calculated MR_D 63.26.

The oxime is a viscous yellow oil that does not crystallize upon cooling. Oxidation of the ketone with potassium permanganate in an alkaline medium yielded 1-methylisophthalic acid with a m.p. of 332°, in addition to 1-methyl-4-isopropylphenylglyoxylic acid, a thick yellow oil, as in the previous synthesis.

0.2133 g substance: 0.6420 g CO_2; 0.1879 g H_2O.
Found %: C 82.09 H 9.75.
$C_{14}H_{20}O$. Calculated %: C 82.35 H 9.80.

When 10 g of the ketone was subjected to Clemmensen reduction with 50 g of amalgamated zinc and 200 ml of hydrochloric acid, we got this hydrocarbon: 1-methyl-2-butyl-4-isopropylbenzene, with a b.p. of 233-235°:

n_D^{10} 1.511; d_{15}^{15} 0.909; MR_D 62.9. $C_{14}H_{22}$. Calculated: MR_D 63.4.

Claus synthesized this same hydrocarbon by reducing 2-butyro-p-cymene with iodine and phosphorus. The constants of this hydrocarbon are given as follows in the literature: b.p. 235°, d^{17} 0.892.

3. Synthesis of 2-Isobutyro-p-cymene

The ketone was synthesized by the method described above from 36 g of isobutyryl chloride, 200 g of cymene, and 45 g of aluminum chloride. Fractionation of the mixture in vacuum yielded the following fractions:

Fraction I: B.p. 100-160° at 7 mm ..... 18 g,
Fraction II: B.p. 165-167° at 7 mm ..... 17 g,
Residue (tar) ..... 6 g.

The yield of the ketone in Fraction 2 was 24.6%, based on the acid chloride. The ketone is a slightly yellowish liquid with the odor of acetophenone. It boils at 257-259° (758 mm):

n_D^{13} 1.504; d_{15}^{15} 0.952; MR_D 63.02. $C_{14}H_{20}O$. Calculated: MR_D 63.26.

0.1134 g substance: 0.3406 g CO_2. 0.0988 g H_2O.
Found %: C 81.91; H 9.65.
$C_{14}H_{20}O$. Calculated %: C 82.35; H 9.80.

Oxidation of the ketone yielded 1-methylisophthalic acid, as in the

preceding cases. Clemmensen reduction of the ketone yielded the hydrocarbon 1-methyl-2-isobutyl-4-isopropyl-benzene, a colorless liquid with a slight, indistinguishable odor and a b.p. of 228-230°; d_{15}^{15} 0.921.

The constants of this ketone are given in the literature as: b.p. 259° and d^{19} 0.957, and a b.p. of 230° and d^{17} 0.916, for the foregoing hydrocarbons.

4. Synthesis of 2-Isovaleryl-p-cymene

The ketone was synthesized, as before, from 270 g of cymene, 60 g of isovaleryl chloride, and 67 g of aluminum chloride. After the cymene had been driven off, the residue was fractionated in vacuum:

Fraction I: B.p. 100-140° at 6 mm ..... 26 g,
Fraction II: B.p. 143-145° at 6 mm ..... 31 g,
Residue (tar) ..... 12 g.

Fraction 2 is the pure ketone, the first fraction being a mixture of the ketone and cymene.

The yield of the ketone was 28.4%, based on the acid chloride. The ketone is a slightly yellowish liquid with a pleasant aroma and a b.p. of 268-270° at atmospheric pressure:

n_D^{20} 1.500; d_{20}^{20} 0.9410; MR_D 67.05. $C_{15}H_{22}O$. Calculated: MR_D 67.48.

0.1406 g substance: 0.4243 g CO_2; 0.1243 g H_2O.
Found %: C 82.29; H 9.81.
$C_{15}H_{22}O$. Calculated %: C 82.57; H 10.09.

The oxime of the ketone, a viscous oil that did not solidify, was synthesized. Methylisophthalic acid, with a m.p. of 231°, was synthesized by oxidation of the ketone with potassium permanganate.

Clemmensen reduction of the ketone yielded a hydrocarbon, 1-methyl-2-isoamyl-4-isopropylbenzene, with a b.p. 244-245°, d_{15}^{15} 0.8920; n_D^{15} 1.502.

The following constants are given for the ketone in the literature: b.p. 270-272°; d^{19} 0.944; with those of the hydrocarbon given as: b.p. 245-246°; d^{17} 0.890.

5. Synthesis of Chloroaceto-p-cymene

The ketone was synthesized, as in the first experiment, from 170 g of cymene, 30 g of chloroacetyl chloride, and 34 g of aluminum chloride. Fractionation in vacuum yielded the following fractions:

Fraction I: B.p. 100-150° at 8 mm ..... 26 g.
Fraction II: B.p. 153-155° at 8 mm ..... 17 g.

The second fraction was the chloroketone. The yield of the ketone was 30.2% in terms of the acid chloride. It is a slightly pinkish liquid with a strongly acrid odor that causes tears:

n_D^{20} 1.520; d_{20}^{20} 1.075; MR_D 59.40. $C_{12}H_{15}OCl$. Calculated: MR_D 58.90.

0.8322 g substance: 0.5532 g AgCl (Stepanov method).
Found %: Cl 16.54.
$C_{12}H_{15}OCl$. Calculated %: Cl 16.67.

Treatment with hydroxylamine hydrochloride yielded the oxime as a thick oil. The following constants are given for this ketone in the literature: b.p. 158-160° at 20 mm; d^0 1.101 [6].

6. Synthesis of 2-Benzoyl-p-cymene

This ketone was synthesized from 110 g of cymene, 23 g of benzoyl chloride, and 22 g of aluminum chloride by the method used above. It should be borne in mind, however, that boiling over the water bath causes considerable tarring of the mixture, and we therefore recommend that heating be done at 50-60° and no higher. Moreover, when the cymene solution of the ketone is washed with water (after decomposition of the reaction mixture), a very stable emulsion is formed, which separates extremely slowly. To avoid formation of this emulsion ether must be added. The residue was fractionated in vacuum after the solvents had been driven off.

Fraction I: B.p. 100-183° at 5 mm ..... 32 g.
Fraction II: B.p. 183-185° at 5 mm ..... 12 g.
Residue (tar) ..... 3 g.

Fraction 1 is a mixture of the ketone and cymene, Fraction 2 being the pure ketone. The yield of the ketone was 25.5%, based on the acid chloride. The ketone is a viscous, yellowish oil with an aromatic odor, which does not crystallize upon standing and chilling to -10°.

n_D^{15} 1.534; d_{15}^{15} 1.0251; MR_D 72.52; $C_{17}H_{18}O$. Calculated: MR_D 73.00.

0.0778 g substance: 0.2438 g CO_2; 0.0525 g H_2O.
0.1336 g substance: 0.4183 g CO_2; 0.0869 g H_2O.
Found %: C 85.23, 85.32; H 7.49, 7.21.
$C_{17}H_{18}O$. Calculated %: C 85.71; H 7.56.

The oxime is an extremely viscous oil, as in the preceding experiments. The position of the carbonyl group in the ketone was determined by oxidizing it by heating it with potassium permanganate in an alkaline medium. This yielded, as in the ketones discussed above, 1-methylisophthalic acid with a m.p. of 231-232°, identified by its characteristic properties. Thus, it may be concluded that the C_6H_5CO group of the benzoyl chloride was also in the ortho position to the cymene methyl radical.

7. Endeavor to Synthesize Tertiary Alcohols from Cymene Ketones by the Grignard Method

20 g of aceto-p-cymene was added to a Grignard reagent, prepared in the usual manner with 3.5 g of magnesium and 22 g of ethyl bromide. Owing to the fact that no outward signs of reaction were manifested, we drove off the ether over a water bath, and then poured in 100 g of anhydrous toluene. The mixture was then heated for 6 hours, with the toluol boiling gently. The mixture was then subjected to the usual treatment. Fractionation yielded the unchanged ketone. Exactly the same results were obtained with 2-isobutyro-p-cymene, when this experiment was repeated with it, the ketone being recovered unchanged. Nor did substitution of ethyl iodide for ethyl bromide in preparing the Grignard reagent yield any better results.

SUMMARY

1. The feasibility of synthesizing cymene ketones without the use of hydrogen sulfide, in a medium consisting of an excess of cymene as a solvent, was investigated.

2. It was shown that under these conditions ketones of cymene can be synthesized with yields that are not inferior to those obtained in a hydrogen-sulfide medium.

3. A new ketone, not previously described in the literature, viz.; 2-benzoyl-p-cymene, has been synthesized.

4. Efforts to synthesize tertiary alcohols from the synthesized ketones by means of a Grignard reaction were fruitless. In all instances the ketone was recovered unchanged.

LITERATURE CITED

[1] Tumbin, Paper Industry, No. 4, 16-20 (1941).

[2] Groggins, Ch. Metallurgical Eng., 34, 291 (1927).

[3] Claus, Lieb. Ann., 150, 508 (1890); 154, 474 (1892); J. prakt. Chem., (2) 43, 536 (1891).

[4] Syntheses of Organic Preparations, ed. Adams, v. IV, p 7 (1936).

[5] G. Meyer. Analysis and Determination of Organic Compounds, p. 325, (1937).

[6] Kungkell, Roritzky, Ber., 33, 3263 (1900); Verley, German Patent 101128; Zbl., 1899, 1, 954.

Received December 27, 1948.

OXY- AND METHOXYAMINO-SUBSTITUTED α,α,DIPHENYL-β,β,β-TRICHLOROETHANE

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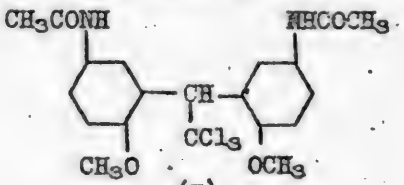
Of the derivatives of α,α-diphenyl-β,β,β-trichloroethane, with substituted oxy and amino groups in various ring positions, only α,α-(4,4'-dioxy-3,3'-diamino)-β,β,β-diphenyltrichloroethane, synthesized from 4,4'-dioxydiphenyltrichloroethane by nitration and subsequent reduction [1], has been known. To prepare isomers of this compound we employed condensation reactions of the acetaminophenols with chloral, expecting to synthesize the corresponding compounds with the hydroxyl groups in the para position to the trichloroethylidene radical (or in the ortho position, if the para position is occupied), since the acetamino group greatly hinders the condensation of aromatic compounds with chloral [2], whereas the oxy and methoxy groups facilitate condensation very readily, sharply orientating it toward the para position [3].

We used ortho, para, and meta acetaminophenols, with the corresponding acetanisidides, for this reaction. It was found that o-acetaminophenol, o-acetanisidide, p-acetanisidide, and m-acetaminophenol condense with chloral in the presence of sulfuric acid, yielding the respective tetra-substituted diphenyltrichloroethanes (I, III, V, IX).



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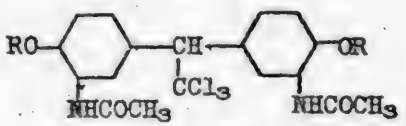
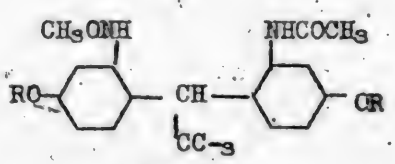


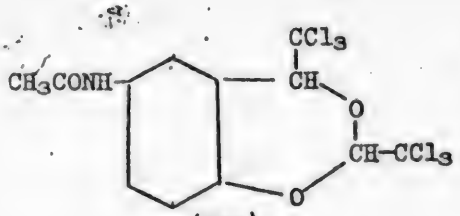
(V, III)



(IX, X)

where: R = H (V, IX); and R = CH_3 (III, X).

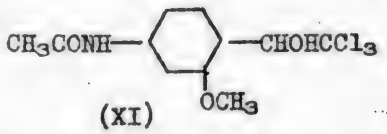
p-Acetaminophenol forms 6-acetoamino-2,4-bis-trichloromethylbenzodioxine:



(VII)

which had been synthesized earlier by Chattaway and Calvet [4] by condensing p-aminophenol with two molecules of chloral and then acetylating the amine.

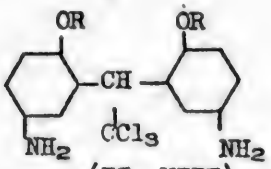
m-Acetanisidide could not be condensed with chloral in the proportions of two molecules of the aromatic compound to one molecule of chloral, the only product being 4-acetamino-2-methoxyphenyl-2,2,2-trichloroethanol-1 (XI):



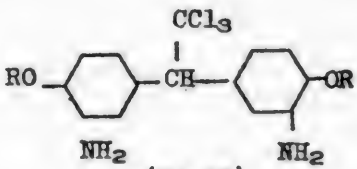
(XI)

Compound (X) was prepared by alkylating p,p'-diacetamino-o,o'-dioxydiphenyltrichloroethane with methyl iodide.

The synthesized acetyl derivatives were converted into the corresponding amines by saponification with hydrochloric acid and isolated as free bases or as their hydrochlorides (II, VI, IV):



(II, VIII)



(VI,IV)

where R = H (VI, VIII); and R = CH_3 (II, IV).

The initial material for synthesizing α,α-(2,2'-dioxy-5,5'-diaminodiphenyl)-β,β,β-trichloroethane (VIII) was the acetyl compound (I), which was re-esterified by boiling with a mixture of acetic and sulfuric acids, with subsequent hydrolysis.

EXPERIMENTAL

I. α,α-(2,2'-Dimethoxy-5,5'-diacetaminodiphenyl)-β,β,β-trichloroethane

16.6 g of p-acetanisidide is added to a mixture of 75 ml of 100% sulfuric acid and 7.5 g of chloral, chilled to -5°, and stirred for 30 minutes with chilling and another 30 minutes at room temperature. Then the reaction mass is poured out over ice, and the substance that separates out is drawn off by suction, carefully washed with water, squeezed out, air dried, and recrystallized from alcohol. The yield is 13 g. M.p. 226-227°. Acicular crystals. They contain alcohol of crystallization. They are nearly insoluble in water, poorly soluble in ether and benzene, and readily soluble in acetone and chloroform.

3.341 mg substance: 6.451 mg CO_2; 1.590 mg H_2O.
3.290 mg substance: 6.391 mg CO_2; 1.571 mg H_2O.

5.351 mg substance: 0.287 ml N_2 (26°, 729.3 mm).
6.556 mg substance: 0.346 ml N_2 (27°, 729.6 mm).
0.1148 g substance: 0.0992 g AgCl.
Found %: C 52.66, 52.98; H 5.32, 5.34.
N 5.86, 5.76; Cl 21.37.
$C_{20}H_{21}N_2O_4Cl_3 \cdot C_2H_5OH$. Calculated %: C 53.27; H 5.47; N 5.65; Cl 21.46.

II. α,α-(2,2'-Dimethoxy-5,5'-diaminodiphenyl)-β,β,β-trichloroethane

2 g of the acetyl derivative is boiled for 6 hours with a reflux condenser. The substance dissolves slowly. The base is recovered from the solution by carefully adding ammonia and chilling. The substance had a m.p. of 74° after being washed with water and dried in an exsiccator. It is readily soluble in most organic solvents and grows dark upon standing. The hydrochloride was prepared by filtering the hot solution after it had been saponified, and then letting it stand overnight. The acicular crystals that separated out were recrystallized from alcohol, m.p. above 230°; thick needles that form rosettes.

7.858 mg substance: 0.446 ml N_2 (20.5°, 735 mm).
7.003 mg substance: 0.393 ml N_2 (20.5°, 735 mm).
Found %: N 6.39, 6.31.
$C_{18}H_{17}O_2N_2Cl_3 \cdot 2HCl$. Calculated %: N 6.25.

III. α,α-(3,3'-Diacetoamino-4,4'-dimethoxydiphenyl)-β,β,β-trichloroethane

11 g of o-acetanisidide is added to a mixture of 35 ml of 100% sulfuric acid and 5 g of chloral over the course of 20 minutes at a temperature not exceeding 2°; stirring is continued for another hour, and the mixture is then poured out over ice. The precipitate that settles out is filtered, washed with water, and air dried. The 17 g of substance recovered is recrystallized from 200 ml of alcohol. The yield is 11 g of a substance with a m.p. of 213-214°. It crystallizes with 1 molecule of alcohol.

5.825 mg substance: 0.297 ml N_2 (27.5°, 734.2 mm).
5.753 mg substance: 0.296 ml N_2 (27.0°, 734.1 mm).
0.2023 g substance: 0.1735 g AgCl.
0.2107 g substance: 0.1800 g AgCl.
Found %: N 5.59, 5.65; Cl 21.22, 21.13.
$C_{20}H_{21}N_2O_4Cl_3 \cdot C_2H_5OH$. Calculated %: Cl 21.46; N 5.65.

IV. α,α-(3,3'-Diamino-4,4'-dimethoxydiphenyl)-β,β,β-trichloroethane

2 g of the preceding acetyl derivative is boiled for 3 hours, after which the well-chilled base is carefully separated out with ammonia, filtered out, whased with water, and dried in a vacuum exsiccator. It dissolves very easily in all organic solvents and does not crystallize out from them. The substance was prepared for analysis from the pure hydrochloride. M.p. 60-61°.

6.675 mg substance: 3.78 ml 0.01N H_2SO_4 (Kjeldahl)
6.400 mg substance: 3.59 ml 0.01N H_2SO_4.
Found %: N 7.93, 7.85.
$C_{18}H_{17}O_2N_2Cl_3$. Calculated %: N 7.46.

The hydrochloride was prepared by saponifying the solution and then evaporating it in vacuum to dryness, the residue being recrystallized from alcohol.

0.2790 g substance: 12.1 ml 0.1N $AgNO_3$
0.1880 g substance: 11.6 ml 0.1N $AgNO_3$.
Found %: Cl 15.38, 15.84.
$C_{18}H_{17}O_2N_2Cl_3 \cdot 2HCl$. Calculated %: Cl 15.81.

V. α,α-(3,3'-Diacetoamino-4,4'-dioxydiphenyl)-β,β,β-trichloroethane

7.5 g of o-acetaminophenol, at a temperature not exceeding 1°, is added to a mixture of 35 ml of 100% sulfuric acid and 4 g of chloral, chilled to -5°, and the whole is stirred for an hour and then poured over ice. The precipitate is filtered out, washed with water, and air-dried. Yield: 10.2 g. It is then recrystallized from 60% alcohol. M.p. 226-227°.

4.292 mg substance: 7.841 mg CO_2; 1.561 mg H_2O.
0.1848 g substance: 0.1817 g AgCl.
0.1801 g substance: 0.1775 g AgCl.
7.807 mg substance: 3.56 ml 0.01N H_2SO_4, (Kjeldahl).
7.599 mg substance: 3.49 ml 0.01 N H_2SO_4.
Found %: C 49.82; H 4.07; Cl 24.32, 24.38; N 6.38, 6.43.
$C_{15}H_{17}N_2O_4Cl_3$. Calculated %: C 50.06; H 3.97; N 6.49; Cl 24.65.

VI. α,α-(3,3-Diamino-4,4'-dioxydiphenyl)-β,β,β-trichloroethane

2 g of the preceding acetyl derivative and 20 ml of concentrated hydrochloric acid are boiled together for 6 hours. The substance gradually enters into solution; the solution is then filtered, and after chilling, the base is precipitated with ammonia. The dried amine is recrystallized from benzene. Decomp. temperature = 152°; it turns black, but does not fuse.

6.012 mg substance: 0.4214 ml N_2 (22°, 732.8 mm).
6.585 mg substance: 0.456 ml N_2 (21.5°, 731.9 mm).
Found %: N 7.82, 7.72.
$C_{14}H_{13}N_2O_2Cl_3$. Calculated %: N 8.06.

The hydrochloride is readily soluble in water.

VII. Condensation of p-Acetaminophenol with Chloral

7.5 g of p-acetaminophenol, 4 g of chloral, and 40 ml of sulfuric acid (d = 1.84) are reacted together at 10°. The mixture is stirred for 2 hours, its temperature gradually rising to 25° and then falling. Four hours later, the reaction mixture is poured into water, and the residue drawn off, washed with water, and air-dried. This yields 7 g of a colorless substance, which is recrystallized from a small quantity of acetone. The m.p. of 205° agrees with that given by Chattaway for 6-acetamino-2,4-bis-trichloromethylbenzodioxine.

7.589 mg substance: 1.92 ml 0.01N H_2SO_4 (Kjeldahl).
7.103 mg substance: 1.80 ml 0.01N H_2SO_4.
Found %: N 3.54, 3.55.
$C_{12}H_8O_3NCl_3$. Calculated %: N 3.4.

VIII. α,α-(2,2'-Dioxy-5,5'-diaminodiphenyl)-β,β,β-trichloroethane

2 g of (2,2'-dimethoxy-5,5'-diacetoaminodiphenyl)-trichlorcethane (I) is boiled for 12 hours with 10 ml of glacial acetic acid and 1 g of 92% sulfuric acid. A crystalline precipitate begins to settle out after about one quarter of an hour has elapsed. The whole mixture is poured into cold water, and the precipitate is filtered out, washed with water, and air-dried. The yield of 1.6 g is insoluble in water or alcohol. The substance is then boiled with 20% hydrochloric acid. Crystals of 5,5'-diamino-2,2'-dioxydiphenyltrichloroethane hydrochloride settle out of the filtered solution when it is chilled; their m.p. is 242°, and they caused an appreciable depression of the melting point

when mixed with the hydrochloride of the corresponding dimethoxy compound.

5.986 mg substance: 0.328 ml N_2 (18.5°, 738 mm).
5.512 mg substance: 0.311 ml N_2 (18.5°, 720 mm).
0.1012 g substance: 4.9 ml 0.1N $AgNO_3$.
Found %: N 6.23, 6.26; Cl 17.16.
$C_{14}H_{13}O_2N_2Cl_3 \cdot 2HCl$. Calculated %: N 6.66; Cl 16.9.

The amine isolated from the pure hydrochloride has a m.p. of 175°. It was recrystallized from benzene, but it rapidly darkens and resinifies.

IX. α,α-(2,2'-Diacetoamino-4,4'-dioxydiphenyl)-β,β,β-trichloroethane

7.5 g of m-acetaminophenol (m.p. 122-123°) is added to a mixture of 70 ml of 100% sulfuric acid and 4 g of chloral during the course of 30 minutes at a temperature that does not exceed 0°; stirring is continued for another 3 hours at 0°, and then the reaction mixture is poured over ice, and the precipitate is drawn off, washed with water, and transferred to ether. The ether solution is desiccated with anhydrous sodium sulfate, and the ether is driven off in vacuum. To recrystallize it, the amorphous precipitate (4 g), which can be easily crushed to a powder, is dissolved by heating it in 40 ml of benzene to which 2 ml of absolute alcohol has been added. The well-formed crystals that are recovered are flat rectangular prisms. M.p. 186°. The substance resinifies when heated with dilute acids.

0.1411 g substance: 0.1432 g AgCl.
4.634 mg substance: 0.280 ml N_2 (22°, 738 mm).
Found %: Cl 25.11; N 6.79.
$C_{18}H_{17}O_4N_2Cl_3$. Calculated %: Cl 24.65; N 6.49.

When we tried to saponify this acetyl derivative, it resinified.

X. α,α-(2,2'-Diacetoamino-4,4'-dimethoxydiphenyl)-β,β,β-trichloroethane

0.5 g of the preceding acetyl derivative in 2 ml of alcohol and 1 g of methyl iodide are added to a solution of sodium alcoholate, prepared with 0.05 g of Na and 3 ml of absolute alcohol. The mixture is heated to gentle boiling (50-60°) over a water bath and poured into cold water after this heating has gone on for three hours. The precipitate that forms is filtered out, washed, and dried. Yield = 0.3 g. It is dissolved in ether to which a few drops of alcohol have been added, and the resulting solution decolored by agitation with charcoal, filtered, and evaporated in vacuum. This yields a noncrystalline substance that is crushed to a powder; it softens at 120°. It is purified by dissolving it in alcohol and precipitating it with water. M.p. 129°.

7.663 mg substance: 0.424 ml N_2 (19°, 736 mm).
Found %: N 6.27.
$C_{20}H_{21}O_4N_2Cl_3$. Calculated %: N 6.1.

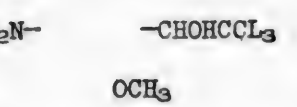
XI. Condensation of Chloral with m-Anisidine.

1,1,1-Trichloro-2-oxy-2-(4-acetamino-2'-methoxyphenyl)-ethane

4.2 g of m-acetoanisidide is added to a mixture of 25 g of 100% sulfuric acid and 2 g of chloral at 0°, and, after 2.5 hours of stirring, the mixture is poured over ice. The precipitate formed is drawn off, washed with water, and recrystallized from alcohol after prolonged standing (3 days). M.p. 179°. The substance dissolves readily in alcohol, acetone, benzene, and acetic acid, but is hardly soluble in ether, and insoluble in water.

6.580 mg substance: 0.283 ml N_2 (19°, 716 mm).
6.127 mg substance: 0.253 ml N_2 (21.5°, 722 mm).
0.2000 g substance: 0.2735 g AgCl.
0.2037 g substance; 0.2795 g AgCl.
Found %: N 4.74, 4.55; Cl 33.83, 33.94.
$C_{11}H_{12}O_3NCl_3$. Calculated %: N 4.48; Cl 34.00.

XII. 1,1,1-Trichloro-2-oxy-(4'-amino-2'-methoxyphenyl)-ethane



Boiling 0.5 g of the preceding substance with 5 ml of 17% hydrochloric acid causes the substance to enter into solution, the amine hydrochloride crystallizing out of the latter when chilled.

6.924 mg substance: 0.280 ml N_2 (19°, 744 mm).
Found %: N 4.63.
$C_9H_{10}O_2NCl_3 \cdot HCl$. Calculated %: N 4.56.

SUMMARY

1. Research has been done on the condensation of ortho, meta, and para acetaminophenols and acetoanisidides with chloral in the presence of sulfuric acid; the 2,2'-dimethoxy-5,5'-diacetamino-, 3,3'-diacetamino-4,4'-dimethoxy-, 3,3'-diacetamino-4,4'-dioxy-, and 2,2'-diacetamino-4,4'-dioxy-α,α-diphenyl--β,β,β-trichloroethanes (II, III, V, and IX) have been synthesized. Condensation of 4-acetaminophenol with chloral yielded 6-acetamino-2,4-bis-trichloromethylbenzodioxine (VII). Condensation of m-acetanisidide with chloral yielded α-(4-acetamino-2-methoxyphenyl)-α-oxy-β,β,β-trichloroethane (XI).

2. α,α-(2,2'-Diacetoamino-4,4'-dimethoxydiphenyl)-β,β,β-trichloroethane (X) was synthesized by methylating the corresponding oxy compound.

3. The amines II, VIII, VI, IV, and XII were prepared by saponifying the acetyl compounds. α,α-(2,2'-Dioxy-5,5'-diaminodiphenyl)-β,β,β-trichloroethane was synthesized by demethylating and saponifying the corresponding dimethoxydiacetamino compound.

LITERATURE CITED

[1] Elbs, J. prakt. Chem. (2), 47, 65 (1893).

[2] Berlin, Shchukina, and Sazanova, J. Gen. Chem., 19, 677, (1949); Burger, Graef, Bailey, J. Am. Chem. Soc., 68, 1725 (1946); Haskelberg, Lavie, J. Am. Soc., 69, 2267 (1947).

[3] Calvet, Mejuto, J. Chem. Soc., 1936, 554.

[4] Chattaway, J. Chem. Soc., 1926, 2726.

Received June 27, 1948.

DETERMINATION OF THE STRUCTURE OF THE DISACCHARIDES

I. DETERMINATION OF THE STRUCTURE OF α-(1,5)-GLUCOSIDO-3-(1,5)-GLUCOSE

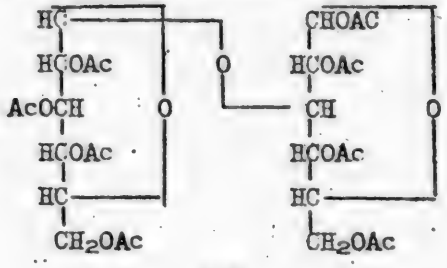
A. M. Gakhokidze

The structure of the disaccharides is determined in various ways. Haworth [1] proposed a methylation method to determine the structure of the disaccharides. In Zemplen's method of decomposition, the reduced monose of the disaccharide is reduced until disaccharides are synthesized that do not yield osazones [2].

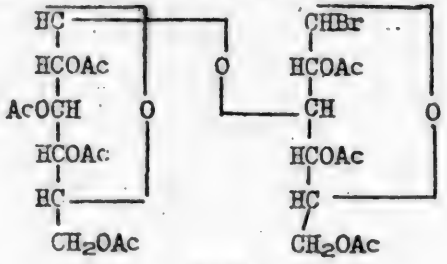
We have elaborated a method for determining the structure of the disaccharides that is based upon the oxidative cleavage of glucaloid unsaturated compounds. In our previous paper [3], we described the synthesis of the disaccharide α-(1,5)-glucosido-3-(1,5)-glucose; determined its structure according to Zemplen. Herein we give the determination of the structure of this glucose by the oxidative cleavage method worked out by us.

α-(1,5)-Glucosido-3(1,5)-glucose was converted into the octacetate (I) by the usual method - reacting it with acetic anhydride in the presence of sodium acetate. The action of hydrogen bromide in glacial acetic acid on the octacetate yielded acetobromoglucosido-3-glucose (II), which is easily converted into hexacetylglucosido-3-glucal (III) by the action of zinc dust in 60% acetic acid.

Saponification of the latter yielded glucosido-3-glucal (IV).



(I)



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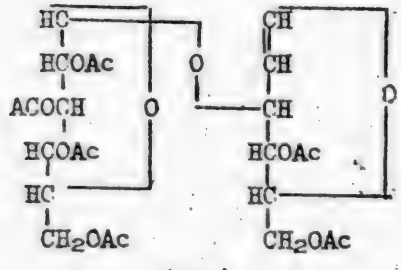

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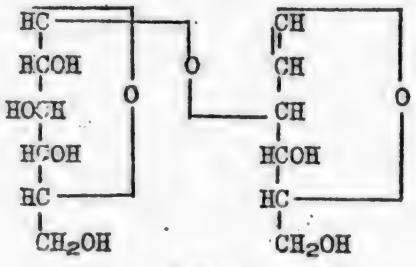
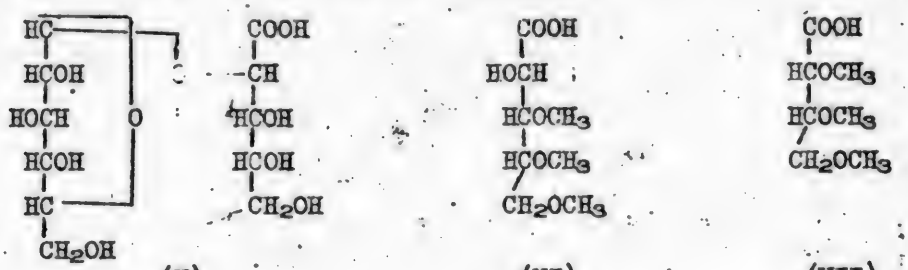


(IV)

Glucosido-2-arabic acid (V) was isolated by oxidizing glucosido-3-glucal with potassium permanganate. Trimethylarabic acid (VI), synthesized by hydrolyzing methylated glucosido-2-arabic acid, yields 2,3,4-trimethylerythronic acid (VII) when it is oxidized by perhydrol.



(V) (VI) (VII)

Hence, the methoxyl groups in trimethylarabic acid occupy the 3,4,5 positions, the 2 position being used for the biose bond.

EXPERIMENTAL

1. Acetobromoglucosido-3-glucose

80 g of glucosido-3-glucose octacetate (m.p. 149°, $[\alpha]_D^{20}$ + 41.3°, in chloroform) was dissolved, with vigorous agitation, in 350 ml of glacial acetic acid, saturated with hydrogen bromide, and the solution produced was set aside to stand for 3 hours at room temperature.

Then the acetobromoglucosido-3-glucose was extracted from the solution with chloroform. Addition of petroleum ether to the concentrated solution caused the colorless crystals of acetobromoglucosido-3-glucose to precipitate out (m.p. 162°, $[\alpha]_D^{20}$ + 11.8° in chloroform). The yield was 58.8 g, i.e., 78% of theory.

0.1379 g substance: 0.0369 g AgBr.
0.1508 g substance: 0.0411 g AgBr.
Found %: Br 11.39, 11.60.
$C_{28}H_{35}O_{17}Br$. Calculated %: Br 11.45.

2. Glucosido-3-glucal

57.5 g of acetobromoglucosido-3-glucose was drenched with 400 ml of 60% acetic acid and 50 g of zinc dust was added; the resulting mixture was then shaken up in an agitator for 2 hours. Hexacetylglucosido-3-glucal was extracted with chloroform after the solution had been diluted with 1.5 liters of water. The residue left after the chloroform was evaporated was recrystallized from ethyl alcohol.

The melting point of the pure product was 109°; $[\alpha]_D^{20}$ + 18.4° (in chloroform). The yield was 42.4 g, or 80% of theory.

0.0847 g substance: 26.5 ml bromine solution (T = 0.0009).
Found %: Br 22.23.
$C_{24}H_{32}O_{15}Br_2$. Calculated %: Br 22.21.

100 ml of a 2% solution of sodium alcoholate was added to a chilled solution of 42.1 g of hexacetylglucosido-3-glucal in 200 ml of chloroform. The resulting mixture was shaken in an agitating machine for 2 hours, after which it was poured into 1 liter of chilled water. The water-alcohol layer was separated

from the chloroform layer and, after it had been neutralized with acetic acid, it was evaporated at reduced pressure (8 mm) down to a thick syrup. The latter crystallized when it was mixed with absolute ethyl alcohol. The melting point of the pure product was 160-162°. The yield was 14.9 g, or 79% of theory.

$\underline{1}$ = 0.5; c = 0.6; α = 10.4°; $[\alpha]_D^{20}$ + 34.8° (in water).

0.1064 g substance: 0.1832 g CO_2; 0.0596 g H_2O.
Found %: C 47.12; H 6.23.
$C_{12}H_{20}O_9$. Calculated %: C 46.72; H 6.48.
0.1024 g substance: 59.9 ml bromine solution (T = 0.0009).
Found %: Br 34.62.
$C_{12}H_{20}O_9Br_2$. Calculated %: Br 34.19.

3. Oxidation of Glucosido-3-glucal

14.4 g of glucosido-3-glucal was dissolved in 200 ml of water. After 100 ml of a 6% solution of potash had been added to the resulting solution, and 8% solution of potassium permanganate was added, with vigorous stirring, over the course of 12 hours. The permanganate was poured into the solution until the color of the reaction medium remained. The filtered solution was evaporated at reduced pressure. The residue was dissolved in a minimum quantity of water, and glucosido-2-arabic acid was precipitated from the solution by basic lead acetate. The precipitate was filtered out, washed, and suspended in water, from which the lead was precipitated with hydrogen sulfide. After the lead sulfide had been removed, the filtrate was boiled with calcium carbonate. The solution was filtered and then concentrated to minimum volume. The addition of absolute alcohol to the concentrated solution caused amorphous flakes of calcium glucosido-2-arabinate to settle out. The yield was 12.1 g, or 68% of theory.

0.1448 g substance: 0.0115 g CaO.
0.1694 g substance: 0.0148 g CaO.
Found %: Ca 5.84, 6.20.
$(C_{11}H_{19}O_{11})_2Ca$. Calculated %: Ca 5.77.

4. Methylation of Glucosido-2-arabic Acid and Hydrolysis of the Resultant Ester

11.8 g of calcium glucosido-2-arabinate was dissolved in 40 ml of water, 100 g of dimethyl sulfate was added, and the resultant mixture was heated to 70°. Then a 25% solution of sodium hydroxide was gradually added so as to keep the reaction medium slightly alkaline. When the addition of the base was complete, the solution was heated for 10-15 minutes. The methylated product was extracted from the solution with chloroform. Desiccation and evaporation of the chloroform yielded a syrup of methyl heptamethylglucosido-2-arabinate. The yield was 11.3 g, or 75% of theory.

0.0987 g substance: 0.4172 g AgI.
Found %: OCH_3 56.19.
$C_{19}H_{36}O_{11}$. Calculated %: OCH_3 56.41.

11.0 g of methyl heptamethylglucosido-2-arabinate was heated to boiling for 15 minutes with 250 ml of a 5% solution of sulfuric acid. The solution was filtered after it had been neutralized with calcium carbonate. The addition of absolute ethyl alcohol to the concentrated solution caused flakes of calcium trimethyl-d-arabinate to settle out. The yield was 4.5 g, or 81% of theory.

0.1125 g substance: 0.0143 g CaO.
Found %: Ca 9.13.
$(C_8H_{15}O_8)_2Ca$. Calculated %: Ca 8.81.

After the calcium trimethylarabinate had been filtered out, the solution was reduced with Fehling's solution, but no osazone was obtained.

4.3 g of calcium trimethylarabinate was dissolved in 300 ml of water. After 1.7 g of iron acetate had been added to the resulting solution, 12 ml of a 30% solution of perhydrol was gradually added, with heating. After the solution had cooled, another 10 ml of perhydrol was added. The solution, filtered through activated charcoal, was mixed with 100 ml of bromine water and left to stand exposed to light for 4 days. After it had been neutralized with calcium carbonate, the solution was filtered and its volume reduced to a minimum. The addition of absolute alcohol to the concentrated solution caused white flakes of calcium trimethyl-d-erythronate to settle out.

0.0722 g substance: 0.0103 g CaO.
0.1029 g substance: 0.0151 g CaO.
Found %: Ca 10.22, 10.52.
$(C_7H_{13}O_5)_2Ca$. Calculated %: Ca 10.15.

After the calcium trimethyl-d-erythronate had been decomposed with the calculated quantity of oxalic acid, and the filtered solution had been evaporated, we got a syrup of trimethyl-d-erythronic acid. The acid was isolated via its phenylhydrazide, with a m.p. of 109°.

0.0958 g substance: 8.9 ml N_2 (16°, 736 mm).
0.1170 g substance: 11.2 ml N_2 (16°, 736 mm).
Found %: N 10.58, 10.89.
$C_{13}H_{20}O_4N_2$. Calculated %: N 10.45.

SUMMARY

1. Glucosido-2-arabic acid was synthesized by oxidizing glucosido-3-glucal with potassium permanganate.

2. 3,4,5-Trimethyl-d-arabic acid has been synthesized.

3. Calcium trimethyl-d-arabinate was converted to trimethylerythronic acid by oxidation with perhydrol.

LITERATURE CITED

[1] W. Haworth and Assoc., J. Chem. Soc., 126, 3094 (1926).

[2] G. Zemplen, Ber., 60, 1555 (1927).

[3] A. Gakhokidze, J. Gen. Chem., 16, 169 (1946).

Received June 18, 1948.

THE REACTIONS OF ORTHO AND PARA DITOLYLMERCURY WITH THE PHENOLS. VII*

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One of the present authors has already shown that some aromatic compounds of mercury can mercurate phenols, forming new organomercury compounds. It was conjectured at the time that this sort of mercuration reaction is a general property of aromatic mercury compounds, the more electronegative the radical that is a constituent of the organomercury compound, the more active being the resulting mercuration. This made a detailed study of the reactions of tolyl derivatives of mercury all the more attractive, since the reactivity of the tolyl radical lies between those of α-naphthol and phenyl in the Karash-Nesmeyanov series; and these latter have already been investigated [1]. Moreover, there is no mention in the literature of the feasibility of reactions of this sort.

The reactions of ortho- and para-ditolylmercury with the following phenols have been investigated: 1) phenol; 2) p-bromophenol; 3) 2,4,6-tribromophenol; 4) o-nitrophenol; 5) p-nitrophenol; 6) 2,4,6-trinitrophenol; 7) resorcinol; 8) hydroquinone; 9) pyrogallol; and 10) α-naphthol.

The reaction was investigated at 150° with no solvent present. As might have been expected, the reactions of the tolyl derivatives of mercury with the phenols fully confirmed the behavior patterns first discovered in the reactions of diphenylmercury with the phenols, thus demonstrating their general applicability to organomercury compounds. The mechanism of mercuration reactions may be explained as follows from the standpoint of the theory of free radicals:

1) $CH_3C_6H_4-Hg-C_6H_4CH_3 \rightleftharpoons CH_3C_6H_4\cdot + CH_3C_6H_4Hg\cdot$

2) $C_6H_5OH + \cdot C_6H_4CH_3 \longrightarrow CH_3C_6H_5 + \cdot C_6H_4OH$

3) $CH_3C_6H_4Hg\cdot + \cdot C_6H_4OH \longleftrightarrow CH_3C_6H_4HgC_6H_4OH$

4) $CH_3C_6H_4HgC_6H_4OH \longrightarrow CH_3C_6H_5 + Hg +$ (oxidation products of the phenols).

As we see it, these equations are an adequate explanation of the well-known fact that the replacement of hydrogen by mercury does not take place at the hydroxyl group, but in the phenol's benzene ring.

When tolyl derivatives of mercury are reacted with substituted phenols (bromophenol and the like), the reaction is terminated in Stage 3) with the formation of new, stable, asymmetrical mercury compounds. When tolyl derivatives of mercury are reacted with unsubstituted phenols (pyrogallol and the like), the reaction goes deeper, and the new organomercury compounds formed decompose further, liberating metallic mercury. The reaction rates of tolyl derivatives of mercury with phenols vary, depending on the nature of the substituents, their number, and their location in the phenol's benzene ring, as has

* Extract from I. A. Chernov's candidate dissertation (1948).

been described in Communication I [1] for diphenylmercury. Tribromophenol and trinitrophenol, for example, form only monomercurated derivatives with the tolyl derivatives of mercury, whereas other mono- and disubstituted phenols give rise to both mono and dimercurated products.

The marked difference between the reactivity of ortho- and para-ditolylmercury is worthy of note. Ortho-ditolylmercury exhibits a high reaction velocity in every case, with respect to the quantity of mercury separating out, as well as to the composition of the new asymmetrical compounds formed. For example, under identical conditions o-ditolylmercury forms dimercurated derivatives with p-bromophenol and p-nitrophenol, whereas p-ditolyl mercury yields mono- and dimercurated derivatives.

I. REACTION OF ORTHO- AND PARA-DITOLYLMERCURY WITH GROUP I PHENOLS

We used 0.2 g of the phenols and of the ditolylmercury. After heating, the contents of the ampoules were heated with benzene until all the unreacted ditolylmercury had been removed, after which they were repeatedly treated with a normal solution of alkali. The residue of metallic mercury was washed with water and dissolved in nitric acid, the mercury being determined in the usual manner.

The formation of toluene was observed in every case.

The results of our experiments on the reaction of para and ortho-ditolyl mercury with the Group I phenols are listed in the table below:

Reaction of Ortho- and Para-Ditolylmercury with Phenols at 150°

Phenol	Quantity of Mercury Liberated	
	From p-ditolyl mercury, %	From o-ditolyl mercury, %
Pyrogallol	71.71	83.49
Hydroquinone	63.85	76.61
α-Naphthol	49.11	88.40
Resorcinol	35.36	77.60
Phenol.....	15.72	56.97
p-Bromophenol.....	0	0
Nitrophenol (p)	0	0
Nitrophenol (o)	0	0
2,4,6-Tribromophenol ..	0	0
2,4,6-Trinitrophenol ..	0	0

II. REACTION OF PARA- and ORTHO-DITOLYLMERCURY WITH GROUP II PHENOLS

1. p-Ditolylmercury and o-Nitrophenol

1 g of o-nitrophenol to 1 g of p-ditolylmercury. Heated to 150° for 6 hours.

The yellow reaction mixture was successively treated with a water-alcohol solution, alcohol, and benzene.

Two products were isolated: from the water-alcohol solution the unreacted o-nitrophenol; from the benzene a light-yellow crystalline compound (0.55 g), with a m.p. of 225-227°.

0.05 g substance: 2.35 ml 0.1N NH_4CNS

Found %: Hg 47.00.

$CH_3C_6H_4HgC_6H_3(OH)NO_2$. Calculated %: Hg 46.69.

Treatment with an alcoholic solution of HCl caused the cleavage of the substance, with the formation of o-nitrophenol (m.p. 43-44°) and p-tolylmercury chloride, with a m.p. of 230-231°(m.p. 233°, according to Nesmeyanov). The substance was dissolved in alkali and recovered unchanged by the action of carbon-dioxide gas. Hence, this substance is p-tolylmercuro-2-nitro-1-hydroxybenzene $CH_3C_6H_4HgC_6H_3(OH)NO_2$.

2. p-Ditolylmercury and p-nitrophenol

1.5 g was taken of each of the initial substances. The reaction conditions and the treatment of the reaction mixture were the same as for the o-nitrophenol. In this test, 3 products were obtained. Unreacted p-nitrophenol (1.65 g) was recovered from the water-alcohol solution. A dark yellow crystalline product with a m.p. of 239° (0.085 g) was recovered from the alcohol.

0.05 g substance: 2.33 ml 0.1N NH_4CNS.
Found %: Hg 46.50.
$CH_3C_6H_4HgC_6H_3(OH)NO_2$. Calculated %: Hg 46.69.

The substance is a monomercurated derivative of p-nitrophenol. The principal product (0.430 g) is obtained in the residue left after treatment with organic solvents, a dark-yellow crystalline compound that did not fuse up to 250°.

0.05 g substance: 2.74 ml 0.1N NH_4CNS.
Found %: Hg 55.60.
$(CH_3C_6H_4Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 55.70.

Cleavage of this product with an alcoholic solution of HCl yielded p-nitrophenol, with a m.p. of 115-116°, and p-tolylmercury, with a m.p. of 232°. The substance was dissolved in alkali and recovered unchanged through the action of gaseous carbon dioxide.

Thus, the principal product of the reaction of p-ditolylmercury with p-nitrophenol is the dimercurated derivative of p-nitrophenol: p-ditolylmercuro-4-nitro-1-hydroxybenzene.

3. p-Ditolylmercury and p-Bromophenol

0.5 g of each of the initial substances was used. They were heated together for 3 hours at 150°. The reaction mixture's treatment was the same as that of the o-nitrophenol. 0.2 g of a pink crystalline substance with a m.p. of 169-170° was recovered from the water-alcohol solution.

0.05 g substance: 2.183 ml 0.1N NH_4CNS.
Found %: Hg 43.66.
$CH_3C_6H_4HgC_6H_3(OH)Br$. Calculated %: Hg 43.27.

The substance was dissolved in alkali, and recovered by the action of gaseous carbon dioxide. Bromination with a solution of bromine in a saturated solution of potassium bromide formed 3,4-dibromo-1-hydroxybenzene, with a m.p. of 78°.

Hence, the mercuration of p-bromophenol with p-ditolylmercury yields a monomercurated derivative: p-tolylmercuro-4-bromo-1-hydroxybenzene.

4. p-Ditolylmercury and 2,4,6-Tribromophenol

0.6 g of 2,4,6-tribromophenol was taken for 0.3 g of p-ditolylmercury. They were heated together for 5 hours at 150°. The reaction mixture was treated with water and then heated with alcohol with a reflux condenser. Two products

were recovered. From water we got the unreacted 2,4,6-tribromophenol (0.3 g). From the alcohol we got a light pink crystalline product (0.12 g), with a m.p. of 186-187°.

0.05 g substance: 1.584 ml 0.1N NH_4CNS.
Found %: Hg 31.68.
$CH_3C_6H_4HgC_6H(OH)Br_3$. Calculated %: Hg 32.27.

Thus, the light-pink crystalline product recovered from alcohol is a monomercurated derivative: p-tolylmercuro-2,4,6-tribromophenol.

5. p-Ditolylmercury and 2,4,6-Trinitrophenol

0.2 g of 2,4,6-trinitrophenol and 0.2 g of p-ditolylmercury were taken. Heating lasted 3 hours at 115°. The treatment given the reaction mixture was the same as that for the o-nitrophenol. The unreacted 2,4,6-trinitrophenol (0.17 g) was recovered from the water-alcohol solution and from the alcohol. From the benzene we recovered a yellow crystalline product with a m.p. of 143-144° with decomposition.

0.05 g substance: 1.917 ml 0.1N NH_4CNS
Found %: Hg 38.34.
$CH_3C_6H_4HgC_6H(OH)(NO_2)_3$. Calculated %: Hg 38.61.

This substance is a monomercurated derivative: p-tolylmercuro-2,4,6-trinitrophenol.

6. o-Ditolylmercury and o-nitrophenol

0.3 g of each of the initial substances was used. Heating lasted 6 hours at 150°. The reaction mixture was treated with a water-alcohol solution, alcohol, and benzene. Two products were recovered. The unreacted o-nitrophenol was recovered (0.05 g) from the water-alcohol solution. After the reaction mixture had been treated with organic solvents, the residue contained the principal reaction product: insoluble, infusible up to 250°, light yellow in color, and crystalline (0.185 g).

0.05 g substance: 2.79 ml 0.1N NH_4CNS
Found %: Hg 55.86.
$(CH_3C_6H_4Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 55.70

Hence, this compound is a dimercurated derivative: di-orthotolylmercuro--2-nitro-1-hydroxybenzene.

7. o-Ditolylmercury and p-Bromophenol

0.3 g of each of the initial reagents was used. Heating lasted 3 hours at 150°. After the reaction mixture had been treated with a water-alcohol solution and alcohol, the residue was heated with a mixture of alcohol, acetone, and benzene and a reflux condenser. A resin was recovered from the water-alcohol solution and from the alcohol. The residue (0.2 g) was light pink in color, insoluble in organic solvents, and infusible up to 250°.

0.05 g substance: 2.683 ml 0.1N NH_4NCS.
Found %: Hg 53.66.
$(CH_3C_6H_4Hg)_2C_6H_2(OH)Br$. Calculated %: Hg 53.19.

Hence, the principal reaction product is a dimercurated derivative: diorthotolylmercuro-4-bromo-1-hydroxybenzene.

8. O-Ditolylmercury and 2,4,6-Trinitrophenol

0.3 g of each of the initial reagents was used. Heating lasted 6 hours

at 150°. The reaction mixture was given the same treatment as in the case of o-nitrophenol. 0.2 g of the unreacted 2,4,6-trinitrophenol was recovered from the water-alcohol solution and the alcohol. After the residue had been treated with benzene, it was heated with alcohol and a reflux condenser. The substance, dark brown in color, had a m.p. of 135-137° with decomposition.

0.05 g substance: 1.916 ml 0.1N NH_4CNS.
Found %: Hg 38.32
$CH_3C_6H_4HgC_6H(OH)(NO_2)_3$. Caclulated %: Hg 38.61.

Thus, the synthesized substance is a monomercurated derivative: o-tolylmercuro-2,4,6-trinitro-1-hydroxybenzene.

9. o-Ditolylmercury and p-Nitrophenol

0.2 g of each of the initial reagents was used. Heating lasted 3 hours at 150°.

The reaction mass received the same treatment as in the case of o-nitrophenol. 0.18 g of the unreacted p-nitrophenol was recovered from the water-alcohol solution and the alcohol. The residue contained a yellow substance that was insoluble in organic solvents and infusible up to 250°.

0.05 g substance: 2.75 ml 0.1N NH_4CNS.
Found %: Hg 55.00.
$(CH_3C_6H_4Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 55.70.

This product is a dimercurated derivative: diorthotolylmercuro-4-nitro-1-hydroxybenzene.

10. p-Ditolylmercury and Resorcinol

2 g of each of the initial reagents was used. Heating lasted 6 hours at 150°. The reaction mixture was red in color. It received the same treatment as in the case of o-nitrophenol. The unreacted resorcinol (1.64 g) was recovered from the water-alcohol solution and from the alcohol. The residue left after treatment with benzene was 1.09 g of a pinkish product, which was a mixture of metallic mercury and a dimercurated compound. After the mercury in the residue had been eliminated, the product was yellow in color, insoluble in organic solvents, and infusible up to 250°.

0.05 g substance: 2.93 ml 0.1N NH_4CNS.
Found %: Hg 58.60.
$(CH_3C_6H_4Hg)_2C_6H_2(OH)_2$. Calculated %: Hg 58.04.

Thus, this substance is a dimercurated derivative: diorthotolylmercuro-1,3-dihydroxybenzene.

SUMMARY

1. It has been established that ortho- and para-ditolylmercury can mercurate the phenols in the same way as diphenylmercury and dinaphthylmercury do.

2. Mono- and dimercurated derivatives are formed when the phenols are mercurated.

3. It has been established that o-ditolylmercury is more reactive than p-ditolylmercury.

LITERATURE CITED

[1] M.M.Koton and T.M.Zorina, J. Gen. Chem., 17, 1220 (1947).

Received June 21, 1948.

RESEARCH ON COMPOUNDS OF HIGH MOLECULAR WEIGHT

XXV. THE PROBLEM OF THE MECHANISM OF LINEAR POLYCONDENSATION REACTIONS

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The linear polycondensation reaction of bifunctional compounds, first investigated by Tilicheyev [1], was subsequently studied in detail by Carothers and his students [2,3], Staudinger [4], Flory [5], and others [11]. These researches established the influence of the structure of the initial components and the experimental conditions upon the velocity, completeness, and course of this reaction.

When bifunctional compounds (such as glycols and dibasic acids) react to form poly esters of linear structure and high molecular weight, the reaction is of the following pattern:

$$xHOOCR''COOH + xHOROH \rightleftharpoons HO(COR'CO - CRO)_xH - (2x - 1)H_2O \qquad (I)$$

As indicated, this reaction is reversible, and the reaction products have functional groups that can react further with the molecules of the initial substances as well as with other links in the chain at any stage of polycondensation. It is therefore thought that, at any stage of completeness of the reaction, the product synthesized consists of a mixture of polymer homologues with chains of varying length, i.e., it is physically heterogeneous.

This assumption is the generally accepted working hypothesis in research on linear polycondensation reactions. No one, however, has as yet described quantitatively the degree of physical heterogeneity, i.e., the proportion of reaction products with different molecular weights.

The first endeavors to achieve a quantitative characterization of the distribution of polycondensation products by means of statistical computation were made by Flory [5] and Schulz [6]. Flory started out with the assumption that the reactivity of a molecule does not depend upon the latter's size, that a reaction takes place solely between functional groups, and that therefore chains grow uninterruptedly, tending toward the complete depletion of the reactive groups. Schulz employed the kinetic equations for esterification and reached similar conclusions. According to Flory and Schulz, the distribution function of the percentages by weight of the fractions of the poly ester consisting of x links (π) may be expressed by the following equation:

$$\pi_x = xp^{x-1}(1 - p)^2, \qquad (II)$$

where x = the number of glycol and acid groups in the poly ester chain; and p = the degree of completion of the reaction, i.e., the ratio of the number of already reacted functional groups to the overall number of reactive groups.

There is not enough experimental material in the literature confirming or disproving Flory's and Schulz's conclusion, though this question is of prime importance for an understanding of the mechanism of polycondensation reactions.

It seemed to us that more concrete data could be gotten on the distribution of the polycondensation products by selecting suitable research objects and making use of methods already known. For this purpose we prepared poly esters by means of the polycondensation of ethylene glycol and decamethylene glycol with adipic acid. The reaction products were investigated to ascertain their fractional composition.

We employed two methods to evaluate the degree of poly dispersion of the products obtained. The first method involved a comparison of the mean values of the molecular weight of the reaction products, these mean values being found by various methods. The second method was based on the fractionation of the poly esters by one of the well-known methods.

It is known that the mean molecular weight of a mixture of polymer homologues, determined cryoscopically, chemically, or by osmosis, depends on the number of articles and is called the "numerical" mean value of the molecular weight $\overline{M}_n$. According to Kraemer and Lansing [7], it may be expressed as a function of the molecular weight and of the percentages of the individual constituents of the mixture of fractions by means of the following formula:

$$\overline{M}_n = \frac{1}{\sum \frac{f_x}{M_x}}, \qquad \text{(III)}$$

where M_x = the molecular weight of the several fractions; and f_x = the proportion of these fractions in the mixture ($\sum f_x = 1$).

The viscosimetric method of determining molecular weight of mixture of polymer homologues depends on the gravimetric ratio of the several fractions, the mean value of the molecular weight being called the "gravimetric" mean. It is expressed by the formula:

$$\overline{M}_w = \sum f_x M_x. \qquad \text{(IV)}$$

The constants in the formulas for computing molecular weight from the viscosity of solutions must be determined by the investigation of narow fractions of the polymer, rather than of the polydispersed mixture, or else the nature of the relationship between molecular weight and solution viscosity must be accurately established throughout the rangeof molecular weights under investigation.

If we are dealing with a monodispersed product, both of the means values of molecular weight are equal:

$$\overline{M}_n = \overline{M}_w = M_x.$$

The numerical value is always smaller than the gravimetric one for a polydispersed product, since at the given stage of completion of the reaction, the value of $\overline{M}_n$ does not depend upon the polydispersion, whereas $\overline{M}_w$ grows with increased polydispersion. The greater the difference between the molecular weights of the individual fractions in the mixture M_{x_1}, M_{x_2}... M_{x_n} and the larger the proportion of these fractions in the whole, the greater will be the ratio $\frac{\overline{M}_w}{\overline{M}_n}$. That is why this ratio may be adopted as an index or coefficient of polydispersion.

We began by checking the correctness of Formulas (III) and (IV) for the mean numerical and gravimetric values of mixtures of poly esters as functions of the fractional composition. For this purpose we took Fraction 2 of poly ester No. 12 (poly ester $^{12}/_{2}$), synthesized from adipic acid and ethylene glycol, with a viscosity molecular weight M_w = 590 and a carboxyl-group molecular weight M_n = 450, and Fraction 2 of poly ester No. 24 (poly ester $^{24}/_{2}$), synthesized from adipic acid and decamethylene glycol. The data for poly ester $^{24}/_{2}$ were: M_n = 5200, M_w = 5000. We then determined the molecular weights of the mixtures with varying proportions of these fractions by viscosimetric and chemical methods. The test results are listed in Table 1 [the notation used in the column headings of Table 1 are those employed in Formulas (III) and (IV)].

TABLE 1

Composition of the mixture, %		Computed			Experimental		
$^{12}/_{2}$	$^{24}/_{2}$	$\bar{M}_w$	$\bar{M}_n$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w$ *	M_n **	$\frac{\bar{M}_w}{M_n}$
00	100	–	–	0.96	5000	5200	0.96
10	90	4600	2540	1.81	4700	2560	1.83
28.4	71.6	3800	1440	2.64	3950	1350	2.93
50.0	50.0	2800	830	3.38	2930	810	3.60
74	26	1650	580	2.85	1790	580	3.09
100	00	–	–	1.31	590	450	1.31

As the data in Table 1 indicate, the experimental values are close to those computed from Formulas (III) and (IV). Hence, these formulas can be used to compute the variation of the mean values of molecular weight with fractional composition. The data of Table 1 are shown in a graph (Fig. 1), the customary mode of representing binary mixtures. As the drawing shows, the mean molecular weight of a mixture, as determined by its viscosity ($\bar{M}_w$) decreases linearly with an increase in the percentage of the fraction with low molecular weight. On the other hand, the molecular weight as determined by the terminal-group method ($\bar{M}_n$), drops sharply when even a small percentage (5-10%) of the fraction with low molecular weight is present.

This pattern also applies to complex mixtures of poly esters. To illustrate this statement, we cite the data in Table 2, where the experimental and computed mean values of $\bar{M}_w$ and $\bar{M}_n$ for complex unfractionated mixtures of poly esters are compared for various values of the polydispersion coefficient. The data were taken from our experiments [8].

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*The viscosity molecular weight was calculated from measurements of the specific viscosity of solutions of the poly ester in benzene at 20 ± 0.02°. The solution concentration was 5 to 10 grams per liter. The Staudinger formula $[\eta]\eta_{sp}/C = K_{aqu}n$, where C - the concentration in grams per liter; $K_{aqu} = 0.93 \cdot 10^{-4}$ (for polyesters in benzene); and n - the number of links in the poly ester chain.

**The terminal-group molecular weight was determined by titration of solutions of the poly ester in a chloroform-methanol mixture with a 0.02N solution of sodium hydroxide in 60% aqueous methanol. The formula used was: $\bar{n}_n = \frac{a \cdot 5000}{k \cdot b}$ where a - the weight of the poly ester mixture; b - the alkali consumed (in ml); and k - the correction applied to the alkali titer.

The mean molecular weights of these mixtures listed in Table 2 were computed from Formulas (III) and (IV) on the basis of experimental data on the determination of molecular weight of the various fractions by viscosimetric, cryoscopic, and chemical methods. As this table shows, the discrepancy between the experimental and computed values does not exceed 10%, i.e., lies within the limits of experimental error.

Thus, determination of the value of $\frac{\bar{M}_w}{\bar{M}_n}$ for unfractionated poly esters of various degrees of polycondensation makes it possible to make an experimental check of the extent to which these data agree with the distribution theory advanced by Flory and Schulz. In fact, if the distribution of the polycondensation products can be expressed by Equation (II), this ratio ought to vary with the stage of completion of the reaction as follows [5]:

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{1+p}{1} \qquad (V)$$

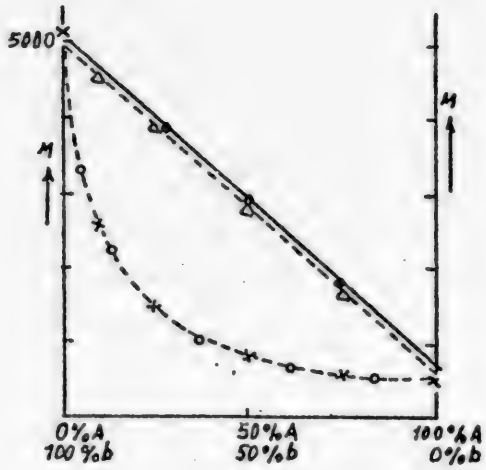

Fig. 1

——— $\bar{M}_w$ calculated,
–^–^–^– $\bar{M}_w$ found,
—o—o— $\bar{M}_n$ calculated,
—x—x—x— $\bar{M}_n$ found.

Table 3 gives the mean numerical and gravimetric values of the molecular weight of poly esters of various degrees of polycondensation found by us. The values of $\bar{M}_w$ and $\frac{\bar{M}_w}{\bar{M}_n}$, computed from Formula (V), are also listed for the sake of comparison.

The notation used in the column headings of the table are those used in Formulas (II), (III), and (IV).

TABLE 2

$\bar{M}_w/\bar{M}_n$ Experimental	$\bar{M}_w$		$\bar{M}_n$	
	Experimental	Computed for the mixture	Experimental	Computed, for the mixture
1.66	700	620	420	410
1.65	930	860	560	600
1.23	1550	1600	1200	1240
1.02	2240	2080	2240	2300
1.05	4200	4330	4100	3860

As seen in the data cited in Table 3, the ratio $\bar{M}_w/\bar{M}_n$ for poly esters with molecular weights above 2000 is close to unity, but is considerably higher for products of low molecular weight. According to Flory's theory, the reverse should be true. This indicates that the actual distribution cannot be expressed by Equation (II). It must also be noted that the polydispersion coefficient expressed by the experimentally found ratio $\bar{M}_w/\bar{M}_n$ is close to unity in all instances. This indicates that the polycondensation products possess a rather low degree of polydispersion.

TABLE 3

Experimental				Computed, by Flory's method	
P	$\bar{M}_n$*	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0.78	420	700	1.66	710	1.78
0.84	560	930	1.65	1000	1.84
0.93	1250	1550	1.22	2400	1.93
0.962	2250	2250	1.00	4400	1.962
0.965	4080	4300	1.05	8000	1.965

The poly esters were subdivided into narrow fractions, differing in molecular weight, for a more thorough investigation of the problem of the degree of polydispersion. Fractionation was effected by fractional precipitation of the poly ester by petroleum ether from a dilute benzene solution (1-2%). The isolated fractions were washed with a mixture of benzene and petroleum ether, used in the same proportions as in the initial precipitation of the poly ester. The temperature was maintained constant (20°, ±0.02°) during the precipitation and separation of the fractions [8]. The fractions thus isolated were dried in vacuum until their weight remained constant.

The results of the fractionation of poly esters at various stages of completion of the reaction are given in Tables 4,5, and 6.

The data of Tables 4-6 are shown graphically in Fig. 2 as differential curves of the mass distribution of the poly ester molecules.

TABLE 4

Fraction No.	Weight of fraction, g	%	Mean molecular weight		
			By viscosity	by carboxyl groups	Cryoscopic method
1	1.164	19.4	2200	2210	2870
2	1.194	20.0	1900	2150	1650
3	2.208	36.8	1520	1740	1470
4	1.254	20.7	1050	1360	1140
5	0.18	3.1	(190) **	(190)**	190
Unfractionated poly ester...	6.00	100.0	1550	1800	1200
Computed from the aggregate of all the fractions			1590	1400	1240

For the sake of comparison, Fig. 2 shows the Flory distribution curve of polycondensation products, computed in accordance with Equation (II) (Curve IV) for P = 0.962, in addition to the experimental curves.

Thus, the experimental data given in Tables 4, 5, and 6, as well as the inspection of the curves indicate that the method of fractionation confirms the hypothesis that the distribution function differs from that of Equation (II). The experimental distribution curve has a more sharply marked maximum π_x. Another characteristic is the absence of any fractions whose molecular weight exceeds the mean value of molecular weight by more than 20%. Our distribution

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* The mean numerical value of molecular weight was determined by three parallel methods: cryoscopically, by determining the carboxyl groups, and by computation from the data of elementary analysis.

** The molecular weights of Fractions 5 and 6 in Tables 4-6 were determined by the cryoscopic method alone.

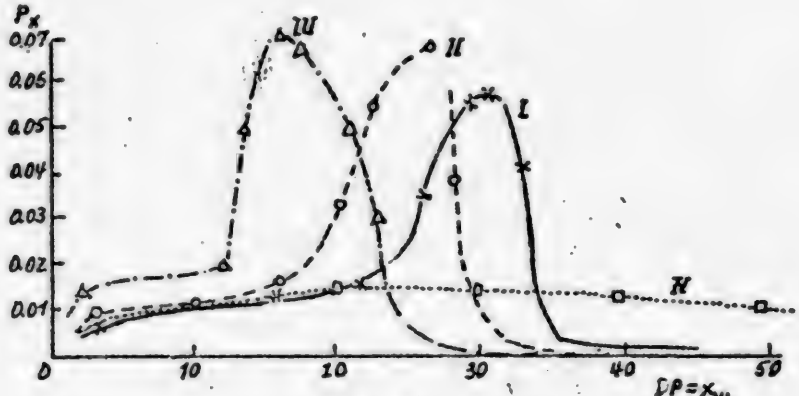

Fig. 2

I – No. 24; P = 0.965. II – No. 8; P = 0.962. III – 7, P = 0.930.
IV – Flory curve for P = 0.962.

curves have sharper maxima at lower degrees of completion of the reaction (P = 0.78; 0.84).

It should be noted that in this case fractionation could be incomplete, as the high concentration of carboxyl and hydroxyl groups makes the formation of associated molecules very likely. There is no doubt that a considerable number of unreacted initial molecules remain in the reaction mixture when the degree of completion of the reaction is low. For instance, we isolated the following quantities of adipic acid at various values of P:

P	Unreacted acid, %
0.5	22.7
0.68	18.0
0.78	7.8
0.84	2.3

At P > 0.9 the poly ester dissolves completely in anhydrous benzene in the cold, which indicates the absence of unreacted adipic acid in gravimetrically determined quantities.

TABLE 5

Molecular Weight and Quantity of Fractions of Poly Ester No. 8

Fraction No.	Weight of fraction, g	%	Mean molecular weight		
			by viscosity	by carboxyl groups	Cryoscopic method
1	2.1236	21.3	2880	3380	3250
2	2.8523	28.5	2350	2700	2600
3	1.3923	13.9	1980	2350	2300
4	1.2974	13.0	1750	2000	1740
5	2.0352	20.4	1400	1500	1340
6	0.3	3.0	(280)	(280)	280
Unfractionated poly ester	10.00	100.0	2240	2240	2200
Computed from aggregate of all fractions			2080	1900	1760

In our opinion, the formation of fairly homogeneous products with the experimentally found distribution function in the linear polycondensation of glycols with dibasic acids and the absence of fractions with very high molecular weights in the mixture of polymer homologues might be explained by the fact that polycondensation reaction consists of a complex system of equilibrium reactions, which might be grouped under the joint heading "polycondensation equilibrium."

TABLE 6

Molecular Weight and Quantity of Fractions of Poly Esters No. 24

Fraction No.	Weight of fraction, g	%	Mean molecular weight		
			by viscosity	by carboxyl groups	cryoscopic method
1	1.7641	17.6	5400	4700	–
2	5.3957	54.0	5000	5200	–
3	0.8926	8.9	3100	4630	–
4	1.7193	17.2	2260	3500	–
5	0.2270	2.3	(460)	(460)	460
Unfractionated poly ester ..	10.00	100.0	4200	4100	–
Computed from aggregate of all fractions	.....		4330	3860	–

We must first admit the possibility that the three following types of poly esters, which differ in the nature of their terminal groups, may be formed simultaneously:

$$xHOOCR'COOH + xHOROH \rightleftharpoons \begin{cases} H(ORO{-}COR'CO)_mOH \ (1) \\ H(ORO{-}COR'CO)_nOROH \ (2) + (2x-1)H_2O \\ HOOCR'CO(ORO{-}COR'CO)_qOH \ (3) \end{cases} \qquad (VI)$$

where $m + n + q + 1 = x$.

With equimolecular proportions of the reaction constituents the probability of the formation of products (2) and (3) is identical, which is why direct chemical investigation of the nature of the terminal groups always yields an aggregate result, corresponding to product (1).

With this assumption, the polycondensation reaction ought to obey the following equations, which are of a general nature, in addition to the basic equation (I).

1. Paralled reaction of the molecules of the glycol and acid with the poly ester chains at the expense of the free functional groups, resulting in gradually lengthening the chain. The water evolved in the process of establishing equilibrium will cause hydrolysis to occur:

$$\text{a) } H(ORO{-}COR'CO)_xOH + HOROH \rightleftharpoons H(ORO{-}COR'CO)_xOROH + H_2O \rightleftharpoons$$
$$\rightleftharpoons H(ORO{-}COR'CO)_mOH + H(ORO{-}COR'CO)_nOROH.$$
$$\text{b) } H(ORO{-}COR'CO)_xOH + HOOCR'COOH \rightleftharpoons HOOCR'CO(ORO{-}COR'CO)_xOH + H_2O \rightleftharpoons \qquad (VII)$$
$$\rightleftharpoons H(ORO{-}COR'CO)_mOH + HOOCR'CO(ORO{-}COR'CO)_nOH$$

---

*The higher fractions and the unfractionated poly ester No. 24 possess negligible solubility in dioxane at 12°., and it was therefore impossible to determine their molecular weight cryoscopically.

where: $m + n = x$.

2. Reaction of the initial molecules with poly ester chains of any length by the mechanisms of acidolysis and alcoholysis reactions taking place simultaneously, resulting in rupturing the long chains:

$$\text{a) } H(ORO{-}COR'CO)_xOH + HOROH \rightleftharpoons H(ORO{-}COR'CO)_mOH + H(ORO{-}COR'CO)_nOROH$$

$$\text{b) } H(ORO{-}COR'CO)_xOH + HOOCR'COOH \rightleftharpoons \tag{VIII}$$

$$\rightleftharpoons H(ORO{-}COR'CO)mOH + HOOCR'CO(ORO{-}COR'CO)nOH,$$

where $m + n = x$.

Equations (VII) and (VIII) apply generally, not only to the reaction of the initial molecules with the poly ester chains, but also to the intermolecular reaction of the poly ester chains of any length, as shown in Equations (IX) and (X):

$$H(ORO{-}COR'CO)_xOH + H(ORO{-}COR'CO)_{x'}OH \rightleftharpoons H_2O + H(ORO{-}COR'CO)_{x+x'}OH \rightleftharpoons$$

$$\rightleftharpoons H(ORO{-}COR'CO)_mOH + H(ORO{-}COR'CO)nOH \tag{IX}$$

$$H(ORO{-}COR'CO)_xOH + H(ORO{-}COR'CO)_{x'}OH \rightleftharpoons H(ORO{-}COR'CO)_mOH +$$

$$+ H(ORO{-}COR'CO)_nOH, \tag{X}$$

where $m + n = x + x'$.

The reactions illustrated by Equations (IX) and (X) take place via acidolysis or alcoholysis reaction mechanisms; they may be termed interchain exchange reactions.

At the same time the interchain exchange reaction may occur by way of reesterification, not involving the terminal groups of the polycondensate (Equation XI):

$$H(ORO{-}CORCO)_p - (ORO{-}COR'CO)_qOH + HO(COR'CO{-}ORO)_r - (CORCO{-}ORO)_sH \rightleftharpoons$$

$$\rightleftharpoons \begin{matrix} H(ORO{-}COR'CO)_p & & (ORO{-}COR'CO)_qOH \\ + & & \\ HO(COR'CO{-}ORO)_r & & (COR'CO{-}ORO)_sH, \end{matrix} \tag{XI}$$

where: $p + q > r + s$; $p + r \approx q + s$.

When the reaction takes place according to any of the foregoing patterns, the probability of rupturing the longer molecules is much greater, owing to the relatively high number of $\frac{x-1}{x}$ bonds, than the probability of rupturing short chains with low values of x.

It should also be noted that the sum of the probabilities of rupture of the poly ester chain somewhere in the middle is much higher than the probability of rupture close to the ends with regeneration of the initial components or products of very low molecular weight. When we adopt the reaction mechanism of dibasic acids and glycols discussed above, the combination of these factors ought to result in the formation of a more monodispersed product than is provided for by current theories. Our experiments corroborate this thesis.

The mechanism of polycondensation equilibrium cited above also explains fully satisfactorily the processes of acidolysis, alcoholysis and aminolysis previously investigated and described [9], and also investigated by Flory [10]. The mechanism of the reaction of bifunctional groups having any other reactive groups should not exhibit any fundamental difference from the case discussed above.

These results are in complete agreement with conjectures proposed by us earlier [11] on the low degree of polydispersion of the products of linear polycondensation.

SUMMARY

1. The mechanism of the linear polycondensation reaction is discussed.

2. On the basis of previous researches by the authors of this paper it is shown that the decisive factor governing the properties of the end products is the polycondensation equilibrium, which comprises several types of simultaneous reversible substitution reactions.

3. Some of the proposed equations lead to the synthesis of chains of higher molecular weight, whereas others involve reactions of acidolysis, alcoholysis, aminolysis, etc., which facilitate exchange between the chains and the constant equalization of the chain lengths.

4. It is shown that the experimentally plotted curves for the distribution of the polycondensation products does not agree with the conclusions of formal statistical "theories". The mass distribution curves for the polycondensation products have sharply marked maxima.

5. The "polydispersion coefficient" of the polycondensation products, expressed as the ratio of the mean gravimetric and numerical values of the molecular weight, is not large.

LITERATURE CITED

[1] M.D.Tilicheyev, J. Russ. Chem. Soc., 57, 143 (1925).

[2] W.H.Carothers, J. Am. Chem. Soc., 51, 2548 (1929).

[3] W.H.Carothers, Van-Natta, J. Am. Soc., 52, 314 (1930); Collected papers of Carothers, New York, 1941.

[4] H. Staudinger, H. Schmidt, J. prakt. Chem., 155, 129 (1940), H. Staudinger, O. Nuss, J. prakt. Chem., 157, 328 (1941).

[5] P. Flory, J. Am. Chem. Soc., 58, 1877 (1936); P. Flory, Chem. Rev., 39, 137 (1946).

[6] G.W.Schulz, Z. phys Chem., A, 182, 127 (1938).

[7] E.O.Kraemer, W.D.Lansing, J. phys. Chem., 39, 153 (1935).

[8] S.R.Rafikov, V.V.Korshak, and G.N.Chelnokova, Izv. USSR Acad., Sci., Div. Chem. Sci., No. 1, 90, (1949).

[9] S.R.Rafikov, V.V.Korshak, and L.N.Pinkina, J. Gen. Chem., 14, 1003 (1944); V.V.Korshak and V.A.Zamyatina, Izv. USSR Acad. Sci., Div. Chem. Sci., 609 (1945). V.V.Korshak, S.R.Rafikov, and V.A.Zamyatina, Acta. Phys. Chem., 21, 723 (1946).

[10] P. Flory, J. Am. Chem. Soc., 62, 2255 (1940); V.V Korshak, S.R. Rafikov, and V.A.Zamyatina, Acta Phys. Chem., 21, 739 (1946).

[11] V.V.Korshak and S.R. Rafikov, Trans. 3rd Conference on Compounds of High Molecular Weight, Izv. USSR Acad. Sci., 1948; V.V.Korshak and V.A. Zamyatina, Doklady USSR Acad. Sci., 58, 101 (1947).

Received February 20, 1948.

SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

IX. SULFONATION OF 1- AND 2-ACETYLPYRROLE

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Our previous reports on the sulfonation of pyrrole derivatives [1] dealt with various methylated pyrroles, which resinify extremely easily when acted upon by acids. Alkyl groups, as we know, reinforce the reactivity of an aromatic ring – in the present instance, the pyrrole ring. Thus, sulfo derivatives of pyrrole and its homologues could be synthesized only by the method proposed by us of sulfonating acidophobic compounds with pyridine sulfotrioxide. In the present paper we report the sulfonation of α- and N-acetylpyrrole. The acetyl group, like any other negative group, facilitates the stabilization of the pyrrole ring, making it less acidophobic.

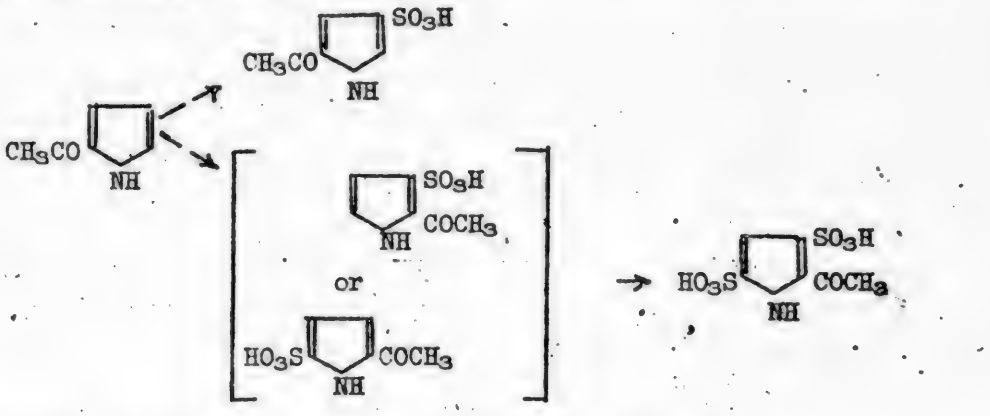
It is noteworthy that α-acetylpyrrole is practically the sole derivative of pyrrole that was ever sulfonated before publication of our researches. In 1885, Ciamician and Silber [2] synthesized the monosulfo acid of 2-acetylpyrrole, which was isolated and analyzed by these authors as its potassium salt, by letting fuming sulfuric acid react with α-acetylpyrrole. The authors give almost no information, however, on the properties of this substance, nor did they determine the point of attachment of the sulfo group. In 1925, B.V.Tronov [3], in apparent ignorance of the work done by Ciamician and Silber, sulfonated α-acetylpyrrole by heating it to 100° for 15-20 minutes with concentrated sulfuric acid. He isolated and analyzed the sulfo acid as its barium salt. But neither did Tronov make a determination of the structure of the synthesized monosulfo acid.

We considered it to be worthwhile to repeat these researches and to determine the structure of the acid that was formed. Moreover, we believed it to be essential to sulfonate 2-acetylpyrrole with the same reagent we used in our previous research, i.e., pyridine sulfotrioxide. We also effected sulfonation of 1-acetylpyrrole with pyridine sulfotrioxide.

Our results were as follows: 2-acetylpyrrole was readily sulfonated by introducing it into 6% oleum in the cold. The barium salt was recovered with a yield of some 75% of theory by treating the mixture with barium carbonate. Analysis showed it to be a salt of a monosulfo acid, which agrees with the observations of Ciamician and Silber, and of Tronov as well.

Structure was determined by oxidizing the salt with chromic acid in a sulfuric-acid medium. If the sulfo group had occupied the alpha position, the oxidation products should have included a maleinimide. But we found not a trace of maleinimide. Treatment of the oxidation products with barium carbonate yielded a salt, the barium content of which corresponded to monosulfomaleinamic acid. This speaks in favor of the sulfonation of 2-acetylpyrrole having taken place at the beta position.

Sulfonation of 2-acetylpyrrole with an excess of pyridine sulfotrioxide at 120-130° in a dichloroethane solution resulted in the formation of a mixture of mono- and disulfo acids in an approximately 1:1 ratio and with an overall yield of 55% of theory. The acids were separated as their barium salts; the barium salt of the disulfo acid was precipitated from an aqueous solution by alcohol, whereas the salt of the monosulfo acid, which is readily soluble in a water-alcohol mixture, remained in the filtrate. Oxidation of both salts yielded monosulfomaleinamic acid. This indicates that one of the beta positions is occupied by a sulfo group in both of these acids. The best way of representing the sulfonation of 2-acetylpyrrole by pryidine sulfotrioxide is by means of the following diagram:



This diagram is based upon the following considerations.

1. Rinkes [4] found that nitration of α-acetylpyrrole produces a mixture of 4-nitro- and 5-nitro-2-acetylpyrrole. The former isomer is the principal reaction product.

Sulfonation is a reaction that is similar to nitration.

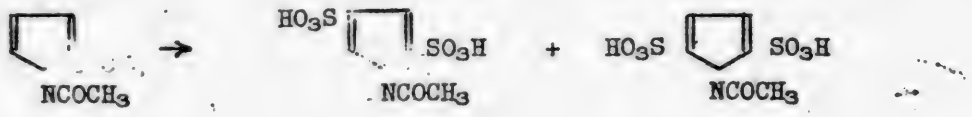
2. Further nitration of the 5-nitro-2-acetylpyrrole yields 3,5-dinitro-2-acetylpyrrole. When 4-nitro-2-acetylpyrrole is nitrated, the acetyl group is replaced by a nitro group. A 4-sulfo acid evidently not prone to further sulfonation, since the second sulfo group would have to enter the ortho position with respect to the first one. On the other hand, a 5-sulfo group (or a 3-sulfo group, respectively) does not impede the further entrance of a second sulfo group in the meta position.

3. Lastly, the high solubility of the barium salt of disulfoacetylpyrrole indicates that the sulfo groups are not in the ortho position toward each other. As a rule, disulfo acids with adjacent sulfo groups have barium salts that are rather insoluble. We find this to be true, in particular, of 2,5-dimethylpyrroledisulfonic-(3,4) and 1,2,5-trimethylpyrroledisulfonic acids.

Our endeavor to sulfonate 1-acetylpyrrole with fuming sulfuric acid was fruitless. This isomer polymerized completely to a red tar, even when chilled. Probably, the acetyl group is split off when oleum is used for sulfonation, the pyrrole that is formed polymerizing naturally.

Sulfonation of 1-acetylpyrrole with pyridine sulfotrioxide yielded a mixture of two disulfo acids. As yet, we have been unable to separate these acids completely. Oxidation of a mixture of their salts with chromic acid in a sulfuric-acid medium yielded N-acetylmaleinimide, which was identical with the synthetic preparation produced by oxidation of pure 1-acetylpyrrole,

together with an acid containing sulfur and nitrogen, its barium and nitrogen content corresponding to N acetylmonosulfomaleinamic acid. With this as a basis, we assign the structure of 1-acetylpyrroledisulfonic-(2,5) acid to one of these acids, and 1-acetylpyrroledisulfonic-(2,4) acid as the most probable structure of the other acid. The high solubility of the barium salt of the disulfo acid leads us to exclude an ortho position for the sulfo groups. Whence, the following sulfonation diagram is the likely one:



EXPERIMENTAL

Sulfonation of α-Acetylpyrrole with Oleum

The initial 2-acetylpyrrole was prepared by reacting acetyl chloride with pyrrolemagnesium bromide (by the method proposed by Adkins and Wolff [5], who improved the method of B. Oddo somewhat).

1.3 g of 2-acetylpyrrole was dissolved in 25 ml of 6% oleum. The solution was poured into water, neutralized with barium carbonate, and filtered to remove the precipitated barium sulfate. The filtrate yielded 2.3 g of the barium salt, or a 75% yield, based on the initial 2-acetylpyrrole. The salt is readily soluble in water, decolorizes bromine water, evolving $BaSO_4$, and is hydrolyzed by boiling with 15% hydrochloric acid, evolving sulfur dioxide. Analysis showed it to be a salt of a monosulfo acid.

5.382 mg substance: 2.433 mg $BaSO_4$
5.895 mg substance: 2.664 mg $BaSO_4$.
Found %: Ba 26.60, 26.58.
$(C_6H_3O_4SN)_2Ba$. Calculated %: Ba 26.71.

Oxidation of the barium salt. 0.6 g of the barium salt of 2-acetylpyrrolesulfonic acid was treated with a mixture of 1 g of CrO_3, 1.3 ml of concentrated sulfuric acid, and 5 ml of water for 20 minutes at 50-60°, and the mixture was set aside to stand at room temperature overnight.

Not even a trace of the maleinimide could be extracted from the reaction mixture by ether. The aqueous solution was neutralized with barium carbonate, and the filtrate evaporated. An acid containing sulfur and nitrogen was recovered. Its barium content indicates it is sulfomaleinamic acid.

6.308 mg substance: 4.880 mg $BaSO_4$.
4.459 mg substance: 2.744 mg $BaSO_4$.
Found %: Ba 41.61, 41.65.
$C_4H_3O_6SNBa$. Calculated %: Ba 41.52.

Sulfonation of α-Acetylpyrrole by Pyridine Sulfotrioxide

1.09 g of 2-acetylpyrrole dissolved in dichloroethane was heated for 8 hours to 100° with 4.77 g of (1:3) pyridine sulfotrioxide, and then for another 3 hours at 120-130°. The dichloroethane was poured off and evaporated; it was found to contain only traces of unreacted 2-acetylpyrrole. The residual mass was treated with an aqueous suspension of barium carbonate, evaporated to dryness and extracted with boiling water. The aqueous extract was evaporated to small volume and precipitated with alcohol. This yielded 1.2 g of a salt (Fraction 1), which

proved to be a disulfo acid upon analysis.

Analysis of Fraction 1

4.313 mg substance: 2.466 mg $BaSO_4$.
10.092 mg substance: 5.633 mg $BaSO_4$.
Found %: Ba 33.65, 33.85.
$C_6H_3O_7S_2NBa$. Calculated %: Ba 33.74.

Oxidation of the barium salt of the disulfo acid. Oxidation was effected as in the previous instance.

3.599 mg substance: 2.549 mg $BaSO_4$.
3.257 mg substance: 2.328 mg $BaSO_4$.
Found %: Ba 42.06, 41.68.
$C_4H_3O_6SNBa$. Calculated %: Ba 41.52.

0.7 g of a salt, (Fraction 2) was precipitated from alcohol after removal of the crystals of Fraction 1; its analysis showed it to be a monosulfo acid.

Analysis of Fraction 2

2.467 mg substance: 1.065 mg $BaSO_4$.
Found %: Ba 25.40
$(C_6H_8O_4SN)_2Ba2H_2O$. Calculated %: Ba 24.95.

Oxidation of the barium salt of the monosulfo acid. 0.1 g of the barium salt was mixed together with 0.17 g of CrO_3, 0.3 g of concentrated sulfuric acid, and 25 ml of water at 50-60°. The mixture was kept at that temperature for 20 minutes. The next day it was extracted with ether. Nothing was found in the ether extract. An acid containing sulfur and nitrogen was recovered from the water after neutralization with barium carbonate. Analysis indicated that the substance was the barium salt of sulfomaleinamic acid.

6.781 mg substance: 4.805 mg $BaSO_4$
3.976 mg substance: 2.790 mg $BaSO_4$.
Found %: Ba 41.73, 41.29.
$C_4H_3O_6NSBa$. Calculated %: Ba 41.52.

Sulfonation of N-Acetylpyrrole

The N-acetylpyrrole was prepared by the method outlined by Ciamician and Dennstedt [6].

B.p. 179-181° (at 763 mm); d_4^{20} 1.044; n_D^{20} 1.5090; MR_D 31.20.
C_6H_7ON. Calculated MR_D 30.69.

1.5 g N-acetylpyrrole dissolved in dichloroethane was heated with pyridine sulfotrioxide for 5 hours to 100° and for another 6 hours at 110-120°. The sulfo mass was treated with an aqueous suspension of barium carbonate, evaporated to dryness, and extracted with hot water. The extract was evaporated to small volume over a water bath and then precipitated with alcohol. This yielded 1.45 g of a salt (Fraction 1). Another 1.55 g of a salt (Fraction 2) was precipitated from the alcohol with ether. Analysis for barium and nitrogen indicated that both fractions corresponded to a disulfo acid of N-acetylpyrrole.

Fraction 1 5.247 mg substance: 3.030 mg $BaSO_4$.
10.676 mg substance: 6.179 mg $BaSO_4$.
Found %: Ba 33.98, 33.89.
$C_6H_3O_7S_2NBa$. Calculated %: Ba 33.74.

Fraction 2

3.354 mg substance: 1.973 mg $BaSO_4$.
4.352 mg substance: 2.555 mg $BaSO_4$.
Found %: Ba 34.62, 34.58.
$C_8H_5O_7S_2NBa$. Calculated %: Ba 33.74.
5.099 mg substance: 0.242 ml N_2 (20°, 728 mm).
Found %: N 5.48.
$C_8H_5O_7S_2NBa$. Calculated %: N 5.30.

Oxidation of the mixture of barium salts of N-acetylpyrroledisulfonic acid. 0.5 g of the barium salt was combined with a mixture of 1 g of CrO_3 and 1.3 ml of concentrated sulfuric acid at 50-60°; the mixture was then kept at that temperature for 20 minutes. The next day it was extracted ten times with a small amount of ether. The ether extract was desiccated over anhydrous sodium sulfate and fused sodium hydroxide. The residue after the ether had been evaporated consisted of white, easily fusible crystals, with a m.p. of 54° The crystals were N-acetylmaleinimide apparently. To confirm this, 1 g of N-acetylpyrrole was oxidized as above. Extraction with ether actually yielded white needles with a m.p. of 54°. A mixed test sample exhibited no depression. Thus, the presence of barium N-acetylpyrroledisulfonate-(2,5) in the initial product undergoing oxidation may be considered as proven.

The aqueous solution was neutralized with barium carbonate. A crystalline salt containing sulfur and nitrogen was recovered from the filtrate by evaporation.

8.217 mg substance: 5.180 mg $BaSO_4$.
7.477 mg substance: 4.694 mg $BaSO_4$.
Found %: Ba 37.10, 36.94.
$C_8H_5O_7SNBa$. Calculated %: Ba 36.87.
5.597 mg substance: 0.190 ml N_2 (25°, 749 mm).
Found %: N 3.83.
$C_8H_5O_7SNBa$. Calculated %: N 3.73.

The barium and nitrogen analysis corresponds to the barium salt of N-acetylsulfomaleinamic acid.

SUMMARY

1. 1- and 2-acetylpyrrole have been sulfonated with pyridine sulfotrioxide.

2. It has been shown that sulfonation of 1-acetylpyrrole yields a mixture of two disulfo acids: 1-acetylpyrroledisulfonic-(2,5) acid and 1-acetylpyrroledisulfonic-(2,4) acid.

3. It has been shown that sulfonation of 2-acetypyrrole yields 2-acetylpyrrolesulfonic-(4) acid and 2-acetylpyrroledisulfonic-(3,5) acid. These acids were isolated and separated as their barium salts.

4. It has been shown that sulfonation of 2-acetylpyrrole with 6% oleum yields 2-acetylpyrrolesulfonic-(4) acid.

LITERATURE CITED

[1] A.P.Terentyev and L.A.Yanovskaya, J. Gen. Chem. 19, 1365 (1949); 19, 538 (1949).
[2] G. Ciamician, P. Silber, Ber., 18, 879 (1885).
[3] B.V.Tronov, Izvestia Tomsk State University, 75, 4 (1925).
[4] I. Rinkes, Rec. trav. chim., 53, 1167 (1934); 56, 1142 (1937).
[5] H. Adkins, J. Wolff, A. Pavlic, E. Hutchinson, J. Am. Chem. Soc., 66, 1923 (1944).
[6] G. Ciamician, M. Dennstedt, Ber., 16, 2353 (1883).

Received June 26, 1948.

THE STRUCTURE OF LEDOL

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Although ledol has been the object of research by many Russian and foreign scientists for more than 100 years, among them: Ivanov [1], Ritsa [2], Trapp [4], Grassmann [cf. 2], Hyelt [5,6], Semmler [7], and Komppa [9,10], we still have no clear notion of its structure.

Grassmann was the first to discover ledol in 1831, in the essential oil of the marsh tea Ledum palustre L. (family Ericaceae), and for a long time the marsh tea was the sole source of this substance, until Hasenfratz [8] discovered ledol in 1924 in the leaves of Sphacele parviflora L. (Family Labiatae).

B. Ritsa [2], who worked in the academic laboratory of A.M. Butlerov, was the first to establish the correct empirical formula of ledol, $C_{15}H_{26}O$; Ritsa's formula was subsequently confirmed by Hyelt and other research workers, various formulas, inexact on the whole, having been given for Ledol prior to Ritsa's investigations. The following specific characteristics of ledol have been known for a long time.

1) Ledol readily splits off water, forming a hydrocarbon, when heated with: a) acetic anhydride (Ritsa) or b) 50% sulfuric acid (Hyelt), or c) when acted upon by phosphorus pentoxide (Ivanov), which may possibly be due to the tertiary position of the hydroxyl group, though no direct experiments to prove the presence of an alcohol group were made.

2) Ledol does not add bromine in an ether solution (Lomidze [3]), nor does it react with permanganate (Hyelt), from which it was concluded that ledol is a saturated compound.

After a series of investigations during the nineteenth century, devoted to ascertaining the composition and properties of ledol, Semmler and Mayer [7] made an effort to establish at least the number of rings ledol has. Determination of its specific gravity, refractive index, and molecular refraction led the authors to conclude that ledol is a bicyclic compound. Doubt was cast upon Semmler's and Mayer's conclusion, however, after the work done by Komppa [9], and subsequently by Komppa and Nymann [10], who came to the conclusion that ledol has a tricyclic structure. As proof of its tricyclic structure, evidence was found confirming the absence of double bonds in ledol (such as, the synthesis of the hydrocarbon ledene, with the composition $C_{15}H_{24}$ and one double bond, when ledol was dehydrated, or the splitting off of water and the formation of dehydroledene when ledol was hydrogenated), whereas ledol should have one double bond, if the bicyclic structure advanced by Semmler and Mayer were correct. This contradiction and several considerations of a theoretical and practical nature convinced me of the need for making an experimental investigation of some of the unclear factors in the chemistry of ledol. Establishing the nature and properties of the products of the dehydration of ledol might not only aid in elucidating its structure, but would also affect further

study of the group of sesquiterpene compounds, especially tricyclic ones.

The ledol used in our research was prepared by freezing the essential oil of marsh tea (Ledum palustre L.). The corresponding oil was obtained by steam-distilling leaves of marsh tea, collected in July 1947 in the environs of Leningrad (near the Kuzmolovo railroad station).

This ledol had a composition close to that of $C_{15}H_{26}O$ and a m.p. of 105-106.5°; it did not react with potassium permanganate in acetone solution, nor did it decolorize bromine in chloroform. Thus it did not differ from the samples of ledol prepared and described previously.

The action of 90% formic acid or 5% alcoholic sulfuric acid upon ledol readily gave rise to hydrocarbons possessing different properties. Thus, heating ledol with formic acid produces a bicyclic hydrocarbon with two double bonds, which I have named leddiene, with a composition of $C_{15}H_{24}$. The properties of leddiene are: d_{20}^{20} 0.9039; n_D^{20} 1.4971; α_D^{17} +35.6°; MR_D 66.06.

On the other hand, heating ledol with 5% alcoholic sulfuric acid yields the tricyclic hydrocarbon ledene, with one double bond and the composition $C_{15}H_{24}$, having an MR_D of 64.46. After distillation over sodium, ledene had the following properties: d_{20}^{20} 0.9278; n_D^{20} 1.5005; α_D^{16} + 48.43°. The specific gravity of this hydrocarbon was close to that of Ritsa's hydrocarbon (d^{18} 0.9237; d^{0} 0.9349)

These results allow of two interpretations. If we accept ledol as a bicyclic compound (in accordance with Semmler and Mayer), the results of the dehydration of ledol with 5% sulfuric acid in an alcohol medium may be explained as due to the fact that the sulfuric acid not only removes the water, but can also isomerize one of the double bonds of ledol or ledene into a third ring.

If we believe that ledol is a tricyclic compound, it must be assumed that 90% formic acid is not only a dehydrating agent, but also possesses the ability to isomerize the tricyclic compound to a bicyclic one, producing an additional double bond in the latter. The latter conjecture was confirmed by experiment. When ledene was heated with formic acid, it was easily converted into leddiene.

Thus our dehydration experiments indicate that ledol and ledene have a tricyclic structure, one of the rings in both of these substances being unstable and subject to rearrangement under the action of formic acid to yield a bicyclic hydrocarbon with two double bonds.

The hydrocarbons ledene and leddiene synthesized by the dehydration of ledol were dehydrogenated by heating them with selenium; it is worthy of note that the isolated $C_{15}H_{18}$ azulenes immediately formed dark, acicular picrates, fusing at 121-122°, when treated with picric acid. The recrystallized picrates exhibited no depression in mixed test samples, i.e., they were identical with one another. In this present instance, what is of interest is not the production of azulenes when leddiene or ledene is dehydrogenated (Kompa obtained an azulene by dehydrogenating ledene as long ago as 1933 and in 1941 Nymann and Mikande [11] demonstrated the feasibility of synthesizing even two different azulenes from a single initial ledene), but the fact that tricyclic ledene and bicyclic leddiene yield identical azulenes (absence of depression in test samples of the mixed picrates). It is possible that the identity of the azulenes is due to the fact that one of the rings of ledene is unstable not only with respect to formic acid, but also to heat, and hence undergoes change during dehydrogenation, forming a bicyclic compound of the leddiene type. This explanation is partially confirmed by the circumstance

that the ledene that does not react during selenium dehydrogenation has its specific gravity reduced, approaching that of leddiene; a drop in the specific gravity of ledene is likewise observed when the latter is distilled under atmospheric pressure or even in vacuum.

In conclusion, let us deal with the problem of the carbon skeleton of ledol.

Komppa, as well as Komppa and Mymann, asserted that ledol has three rings, two of which were six-membered and one cyclopropanic. The latter is located either within or outside one of the six-membered rings. This hypothesis was based upon the synthesis of a naphthalene derivative (cadalene) and an azulene when ledene was dehydrogenated for a long time (38 hours) at 300°.

The cadalene found by Komppa among the products of the dehydrogenation of ledene was nevertheless not a convincing proof of the presence of two six-membered rings in ledene or ledol, since the azulenes could be isomerized to naphthalene derivatives under high temperature for 38 hours. Thus, for example, Heilbronner and Wieland [12] report that the simplest azulene, $C_{10}H_8$, is rearranged into its isomer, naphthalene, when heated to 270° and higher. A very large quantity of naphthalene is formed when the azulene is heated to 330° for 48 hours.

In our experiments on the dehydrogenation of ledene and leddiene, no naphthalene derivatives (such as cadalene) were found in either case after 4 hours, whereas azulene, with a composition of $C_{15}H_{18}$, always appeared as soon as the hydrocarbon was heated with selenium, though in a yield that did not exceed 10%. We found the substances that did not react with selenium to be close to the initial hydrocarbon; they again yielded azulene when redehydrogenated.

The results of our experiments on the dehydrogenation of ledene and leddiene justify the assumption that ledol has the basic skeleton of an azulene (a combination of five- and six-membered rings). Our research is being continued.

EXPERIMENTAL

Synthesis and Properties of Ledol

The essential oil of marsh tea (Ledum palustre L.) was produced by distilling freshly chopped leaves of the plant for two hours with steam.

The yield of the oil was 0.7%, but exceeded 1% at times. The oil was jellylike at 12-14° and almost solidified at -20°. A considerable portion of the ledol in the oil could be separated by suction, but nearly complete separation of the ledol required fractional distillation of the oil and freezing of the higher-boiling fractions.

Repeated recrystallization of the crude ledol from ethyl alcohol yielded snow-white needles of various sizes, possessing a m.p. of 105-106.5°.

The yield of ledol from the oil was 8-10%. In its pure state ledol has no odor.

0.1403 g substance: 0.4169 g CO_2; 0.1480 g H_2O.
0.1373 g substance: 0.4082 g CO_2; 0.1457 g H_2O.
Found %: C 81.04, 81.08; H 11.72, 11.78.
$C_{15}H_{26}O$. Calculated %: C 81.08; H 11.71.

Tserevitnikov hydroxyl determination (xylene as solvent).
0.1406 g substance: 13.55 ml CH_4 (0°, 760 mm).
$C_{15}H_{25}OH$. Calculated %: 14.2 ml CH_4.

The ledol had only slight optical activity: α_D^{17} +0.5° (in a 10% alcohol solution), whence $[L]_D^{17}$ +5°. (According to Hyelt $[L]_D$ +7.98°). The stability of ledol toward alkalies was shown by heating it (1 g) for 3-4 hours over a water bath with a 5% alcoholic solution of KOH (10 ml). The ledol was recovered unchanged after this heating (no depression when mixed with the original ledol).

Heating ledol with acids in aqueous or alcoholic solutions (such as dilute sulfuric or hydrochloric, or glacial acetic and 90% formic acids) demonstrated the instability of ledol toward acids. As a rule, ledol is not recovered, a noncrystalline liquid substance being formed.

The ledol (0.5 g) was quite stable when acted upon by a solution of potassium permanganate (0.5 g) in acetone (15 ml). Practically no $KMnO_4$ was consumed during this oxidation, and the ledol was recovered unchanged (no depression when mixed with the original ledol). Nor is ledol oxidized when titrated with benzoyl peroxide (0.15N) in chloroform solution. After 20 hours the titer of the perbenzoic acid remained unchanged.

When a solution of bromine in chloroform was allowed to act upon a chloroform solution of ledol, the bluish-violet color that is typical of substances with an azulene carbon skeleton did not appear, nor was the bromine decolorized; but the bluish-violet color of the solution is readily observed if the reaction is effected in an acetic-acid medium instead of in a chloroform solution.

Dehydration of Ledol by Formic Acid. Synthesis of Leddiene.

9.5 g of ledol was mixed with 15 ml of 90% formic acid and heated to gentle boiling for 15 minutes. The colored reaction mixture, in two layers, was chilled and diluted with water (50 ml). The oily layer was separated in a separating funnel, washed with water and a dilute soda solution, and steam distilled.

This yielded 8.4 ml of a slightly colored liquid with the following properties: d_{20}^{20} 0.9027; n_D^{20} 1.4971.

The oil became completely colorless after one distillation over Na and two distillations without Na. The properties of the redistilled oil were practically identical with those listed above:

B.p. 103-106° (3 mm); d_{20}^{20} 0.9039; n_D^{20} 1.4971; α_D^{17} +35.6° (in a tube 2.5 cm long α_D^{17} + 8.9°).

0.1760 g substance: 0.5688 g CO_2; 0.1875 g H_2O.
Found %: C 88.14; H 11.83.
$C_{15}H_{24}$. Calculated %: C 82.23; H 11.77.
Found : MR_D 66.06.
$C_{15}H_{24}F_2$. Calculated : MR_D 66.136.

When treated with bromine in a chloroform and acetic acid solution the synthesized hydrocarbon, leddiene, turns the solution an intense violet. Leddiene is soluble in most of the usual solvents, but it is practically insoluble in water, and only slightly soluble in ethyl alcohol.

Dehydrogenation of Leddiene

2 g of selenium was added to 2.5 g of leddiene, and the mixture was heated to a gentle boil for four hours. The mixture turned an intense violet. After cooling, the mixture was steam distilled. The recovered oil was extracted with low-boiling gasoline (60-90°), the gasoline solution turning

violet. The gasoline solution became nearly colorless after it had been shaken up 2 or 3 times with 50% H_2SO_4 (10 ml of the acid being used each time), the sulfuric-acid extracts being colored a brownish-red. Five times its own volume of cold water was added to the sulfuric-acid extract, and the mixture was extracted with freshly prepared ethyl ether until new batches of the ether no longer turned violet in color. The ether solution was dried with Glauber salt, the ether driven off, and a solution of 0.2 g of picric acid in 2 ml of absolute alcohol added to the approximately 0.2 g of residue -- a violet-colored oil. A continuously solidified picrate (dark needles) formed at once.

The picrate was recrystallized from alcohol; after a second recrystallization it had the constant m.p. of 121-122°.

The picrate of the leddiene's azulene causes no depression when mixed with a picrate of the azulene synthesized by dehydrogenating the high-boiling fraction of the essential oil of the roots of Ferula pyramidata Eug. Kor. As the azulene from the essential oil has the formula $C_{15}H_{18}$ according to analysis, the azulene from leddiene must be assigned the same constitution. After the azulene had been eliminated, the oil remaining in the gasoline solution was recovered by driving off the gasoline and steam distilling the residue. The nearly colorless oil that was recovered had the following constants: d_{20}^{20} 0.9027; n_D^{23} 1.4935; i.e, constants that were close to those of the initial leddiene. Repeated dehydrogenation of the unreacted leddiene again yielded a small amount of the azulene as before, which yielded the same picrate m.p. (121-122°).

Dehydration of Ledol with 5% Sulfuric Acid. Synthesis of Ledene

5 g of ledol was dissolved in 18 ml of absolute ethyl alcohol, and 3 ml of an alcoholic solution of sulfuric acid, consisting of 2 ml of absolute alcohol and 1 ml of H_2SO_4 (sp. gr. 1.84), was added to the solution. The transparent mixture was heated for a few minutes over a water bath until it turned cloudy and separated into two layers. Then 100 ml of water was added to the cooled mixture, the oil was extracted by agitating the mixture with ethyl ether, the ether was driven off, and the residue was steam distilled. This yielded 4.5 ml of a colorless liquid -- ledene, which had the following properties: d_{20}^{20} 0.9315; n_D^{20} 1.5002. MR_D 64.46. $C_{15}H_{24}F$. Calculated: MR_D 64.40.

Redistillation over Na yielded a liquid with properties that were only slightly different:

B.p. 110-113° (3 mm); d_{20}^{20} 0.9278; n_D^{20} 1.5005; α_D^{18} + 48.43°.

0.1024 g substance: 0.3298 g CO_2; 0.1092 g H_2O.

Found %: C 87.83; H 11.85.

$C_{15}H_{24}$. Calculated %: C 88.23; H 11.77.

The ledene recovered after redistillation over sodium had a slightly higher molecular refraction that that which had not been redistilled:

Found: MR_D 64.72.

$C_{15}H_{24}F$. Calculated: MR_D 64.403.

$C_{15}H_{24}F_2$. Calculated: MR_D 66.13.

The solution is colored violet almost instantaneously when a few drops of a dilute solution of bromine in chloroform or acetic acid are added to the corresponding solution of ledene.

Dehydrogenation of Ledene

1.5 g of ledene was mixed with 1.5 g of selenium, and the mixture was heated to a gentle boil for 4 hours. The liquid, which was an intense violet

in color, was extracted with low-boiling gasoline (50-70°), and the solution was then steam distilled. The gasoline solution was then shaken up with 90% phosphoric acid until the gasoline layer lost its color, ten times its own volume of water was added to the phosphoric-acid solution, and the azulene that separated out was extracted with freshly distilled ethyl ether. The ether extract was dried with Glauber salt, the ether was driven off, and the residue of 0.1 g was dissolved in 0.5 ml of absolute alcohol. Adding 0.1 g of picric acid dissolved in 0.5 ml of alcohol to the solution thus obtained yielded the picrate as dark needles. M.p. 121-122° (from alcohol). This picrate caused no depression when mixed with the picrate of azulene prepared by dehydrogenating leddiene. After the azulene had been extracted from the gasoline solution, a nearly colorless oil was found in the gasoline; it was easily separated by driving the gasoline off over a boiling water bath. The oil was then steam distilled (yield = 1.1 ml); its b.p. was 78-111° (3 mm); d_{20}^{20} 0.9096; n_D^{20} 1.4934, which does not bear out the assumption that cadalene is present in the oil. When the oil was again dehydrogenated with selenium, it yielded azulene again.

Action of 90% Formic Acid on Ledene. Synthesis of Leddiene.

1.4 g of ledene was mixed with 5 ml of 90% formic acid and then heated to a gentle boil. The mixture turned blue and then red, and changed from a two-layer mixture to a homogeneous one toward the end of the reaction. Within 15 minutes the mixture was cooled and diluted with water until the layers clearly separated, and the upper oily layer removed in a separating funnel, washed with water and a dilute soda solution, and steam distilled. This yielded 1.2 ml of a colorless, mobile liquid, whose properties resembled those of leddiene after it had been desiccated with Glauber salt.

B.p. 101-105° (3 mm); d_{20}^{20} 0.9038; n_D^{20} 1.4975. MR_D 66.05.
$C_{15}H_{24}F_2$. Calculated: MR_D 66.136.

0.1114 g substance: 0.3603 g CO_2; 0.1191 g H_2O.
Found %: C 88.20; H 11.87.
$C_{15}H_{24}$. Calculated %: C 88.23; H 11.77.

Thus, this synthesized hydrocarbon does not differ in its properties or composition from the leddiene previously described.

SUMMARY

1. Ledol was found to behave differently toward acids:

a) Dehydration of ledol, $C_{15}H_{26}O$, with a m.p. of 105-106.5°, by 5% sulfuric acid in absolute ethyl alcohol causes the formation of the hydrocarbon ledene, $C_{15}H_{24}$, with properties that correspond to those of a tricyclic hydrocarbon with a single double bond;

b) Dehydration of ledol by 90% formic acid leads to the formation of the hydrocarbon leddiene, $C_{15}H_{24}$, with properties that correspond to those of a bicyclic hydrocarbon with two double bonds.

2. Like ledol, the hydrocarbon ledene is converted to leddiene by the action of 90% formic acid.

3. When ledene and leddiene are dehydrogenated by selenium, they form the same hydrocarbon of the azulene series, with the composition $C_{15}H_{18}$, which forms a picrate with a m.p. of 121-122°.

4. Experimental results indicate that ledol is a tricyclic tertiary alcohol, which may be classed as a derivative of the azulene series.

LITERATURE CITED

[1] N. Ivanov, Pharm. Zeitschr. f. Russl., 19, 577 (1876).

[2] B. Ritsa, J. Russ. Phys. Chem. Soc., 19, 1, 319 (1887).

[3] K. Lomidze, Pharm. Jour., 29, 1037 (1903).

[4] I. Trapp, Ber., 8, 542 (1875).

[5] E. Hyelt and Uno Collan, Ber., 15, 2500 (1882).

[6] E. Hyelt, Ber., 28, 3087 (1895).

[7] F.W. Semmler and E. Mayer, Ber., 45, 1384 (1912).

[8] M.V.Hasenfratz, C.r., 187, 903 (1924).

[9] G. Komppa, Ch. Zbl., 11, 3121 (1933).

[10] G. Komppa and G. Nymann, C.r., Trav. Lab. Carlsberg, 22, 272 (1938).

[11] G. Nymann and I. Mikande, Ch. Zbl., 1, 3376 (1941); Ber. v. Sch. 122 (1941).

[12] E. Heilbronner and K. Wieland, Helv., XXX, 947 (1947).

Received March 13, 1948.